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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: <b>PCT/JP97/01955</b> (22) International Filing Date: 9 June 1997 (09.06.97) (30) Priority Data:  <table border="0"> <tr> <td>8/146981</td> <td>10 June 1996 (10.06.96)</td> <td>JP</td> </tr> <tr> <td>8/153718</td> <td>14 June 1996 (14.06.96)</td> <td>JP</td> </tr> <tr> <td>8/209587</td> <td>8 August 1996 (08.08.96)</td> <td>JP</td> </tr> <tr> <td>9/13655</td> <td>28 January 1997 (28.01.97)</td> <td>JP</td> </tr> </table> <p>(71) Applicant (for all designated States except US): <b>HITACHI, LTD. [JP/JP]</b>; 6, Kanda Surugadai 4-chome, Chiyoda-ku, Tokyo 101 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): <b>HANAOKA, Hiroshi [JP/JP]</b>; Kodairajousui Hausu 205, 8-1, Jousuiminami-cho 3-chome, Kodaira-shi, Tokyo 187 (JP). <b>KURODA, Osamu [JP/JP]</b>; 3-13, Hanayama-cho 1-chome, Hitachi-shi, Ibaraki 316 (JP). <b>DOI, Ryouta [JP/JP]</b>; 308-2, Nukadaminamigou, Naka-machi, Naka-gun, Ibaraki 311-01 (JP). <b>IIZUKA, Hidehiro [JP/JP]</b>; 1-306, Ishikawa-cho 6-chome, Hitachinaka-shi, Ibaraki 312 (JP). <b>OGAWA, Toshio [JP/JP]</b>; 31, Higashihoncho 3-chome, Takahagi-shi, Ibaraki 318 (JP). <b>YAMASHITA, Hisao [JP/JP]</b>; 22-7, Hanayama-cho 2-chome, Hitachi-shi, Ibaraki 316 (JP). <b>AZUHATA, Shigeru [JP/JP]</b>;</p> </p>		8/146981	10 June 1996 (10.06.96)	JP	8/153718	14 June 1996 (14.06.96)	JP	8/209587	8 August 1996 (08.08.96)	JP	9/13655	28 January 1997 (28.01.97)	JP	<p>40-18, Ishinazaka-cho 2-chome, Hitachi-shi, Ibaraki 319-12 (JP). <b>KITAHARA, Yuichi [JP/JP]</b>; 2031-814, Tsuda, Hitachinaka-shi, Ibaraki 312 (JP). <b>HIRATSUKA, Toshifumi [JP/JP]</b>; Yukou-ryo B-302, 1477-2, Tabiko, Hitachinaka-shi, Ibaraki 312 (JP). <b>OKUDE, Kojiro [JP/JP]</b>; 19-4-303, Ishinazaka-cho 1-chome, Hitachi-shi, Ibaraki 319-12 (JP). <b>SHINOTSUKA, Norihiro [JP/JP]</b>; Tabiko AP 5-303, 940-38, Tabiko, Hitachinaka-shi, Ibaraki 312 (JP). <b>MANAKA, Toshio [JP/JP]</b>; 3600-38, Higashiishikawa, Hitachinaka-shi, Ibaraki 312 (JP). (74) Agents: <b>TAKADA, Yukihiro et al.</b>; 1-48, Saiwai-cho 2-chome, Hitachi-shi, Ibaraki 317 (JP). (81) Designated States: <b>AU, CA, CN, KR, LK, MN, NZ, US, VN</b>, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>
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<p>(57) Abstract An exhaust gas purification apparatus for use in an internal combustion engine comprises an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub> gas passes and a catalyst so disposed in the exhaust gas duct that it contacts with the exhaust gas. The catalyst chemically adsorbs NO<sub>x</sub> under the condition that a stoichiometric amount of a gaseous oxidizing agent present in the exhaust gas is larger than that of a gaseous reducing agent present in the exhaust gas for reducing NO<sub>x</sub>, while NO<sub>x</sub> being adsorbed is catalytically reduced in the presence of the reducing agent under the condition that the stoichiometric amount of the oxidizing agent is not larger than that of the reducing agent. Thereby, NO<sub>x</sub>, the lean burn exhaust gas in the engine can be effectively made harmless.</p>														

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## DESCRIPTION

EXHAUST GAS PURIFICATION APPARATUS OF INTERNAL  
COMBUSTION ENGINE AND CATALYST FOR PURIFYING EXHAUST GAS  
5 OF INTERNAL COMBUSTION ENGINE

## TECHNICAL FIELD

The present invention relates to a purification  
apparatus of an exhaust gas which is discharged or  
10 emitted from an internal combustion engine such as an  
automobile and, particularly relates to a purification  
apparatus for an exhaust gas and a catalyst for  
purifying an exhaust gas from an internal combustion  
engine which can be operated under a lean air-fuel ratio  
15 (a lean burn) and from an automobile which mounts that  
lean burn internal combustion engine.

## BACKGROUND ART

An exhaust gas discharged from an internal combustion  
20 engine such as an automobile includes carbon monoxide (CO),  
hydrocarbon (HC) and nitrogen oxide (NOx) etc.. Such CO,  
HC and NOx form air pollution materials and they have a  
bad influence on human body and further cause a problem  
where it disturbs the growth and the development of  
25 plants.

Accordingly, up to now a great deal of effort has  
gone into the reduction of an amount of pollutant, and  
in addition to the reduction of a generation amount of  
the pollutant according to an improvement of a  
30 combustion method in the internal combustion engine, a  
development for a method for purifying the discharged or  
the emitted exhaust gas using a catalyst etc. and it can  
obtain a steady result.

As to a gasoline engine vehicle, a main current is a method for employing a three component catalyst where platinum (Pt) and rhodium (Rh) are main active components and the oxidation of HC and CO and the reduction of NOx are carried out at the same time and the above air pollution materials are converted to harmless materials.

Herein, from the characteristics of the three component catalyst, the three component catalyst acts effectively only to the exhaust gas which generates according to the combustion at a vicinity of a stoichiometric air-fuel ratio, namely it is called as a "window".

By the above reasons, in the conventional technique, though the air-fuel ratio can fluctuate in accordance with an operation condition of the automobile. A fluctuation region is principally adjusted at a vicinity of the stoichiometric air-fuel ratio which is a ratio between A (weight of air) and F (weight of fuel) being about 14.7 in case of the gasoline. Hereinafter, in the present specification, the stoichiometric air-fuel ratio is represented by  $A/F = 14.7$  but this value varies in accordance with kinds of the fuels.

However, in case where the engine is operated under a lean air-fuel ratio in comparison with the stoichiometric air-fuel ratio atmosphere, the fuel consumption can be improved. Therefore, the development for the lean burn combustion technique is promoted, in recently the automobile in which the engine is combusted under the lean area having the air-fuel ratio of more than 18 appears.

However, when a current three component catalyst is adopted for the purification of the lean burn exhaust

gas, the oxidation purification with respect to HC and CO is performed but the reduction purification with respect to NOx is not effectively performed.

Accordingly, to promote an application of the lean burn system for a large scale size vehicle and an enlargement of the lean burn combustion time (an enlargement of an application operation area of the lean burn system), it is necessary to develop the exhaust gas purification technique which is suitable to the lean burn system.

As a result, the exhaust gas purification technique suitable to the lean burn system, namely the development of a technique for purifying HC, CO and NOx where a large quantity of oxygen (O<sub>2</sub>) is included in the exhaust gas, in particularly a development of a technique for purifying NOx is promoted vigorously.

In Japanese patent laid-open publication No. 61,708/1988, it has proposed a technique where HC is supplied to an upstream of a lean burn exhaust gas and an ability for a catalyst is drawn out, where oxygen (O<sub>2</sub>) concentration in the exhaust gas is lowered to a concentration area for effectively functioning the catalyst.

In Japanese patent laid-open publication No. 97,630/1987, Japanese patent laid-open publication No. 106,826/1987 and Japanese patent laid-open publication No. 117,620/1987, it has proposed a technique that N included in the exhaust gas (after the conversion of an easily absorbable NO<sub>2</sub> by oxidizing NO) is absorbed and removed by contacting to a catalyst having NOx absorbing ability. After at a time where an absorption efficiency lowers by stopping a passing-through of the exhaust gas an accumulated NOx is reduction-removed using H<sub>2</sub>, HC

included in a methane gas and a gasoline etc. and NOx absorbing ability of the catalyst is regenerated.

Further, in WO 93/07363 and WO 93/08383, it has proposed an exhaust gas purification apparatus in which NOx absorbent absorbs NOx from a lean exhaust gas and when an oxygen concentration in the exhaust gas is lowered NOx absorbent discharges the absorbed NOx, is arranged at an exhaust gas flow passage. And the exhaust gas absorbs NOx during the lean atmosphere and the absorbed NOx is discharged by lowering O<sub>2</sub> concentration in the exhaust gas which flows into a NOx absorbent.

However, in Japanese patent laid-open publication No. 61,708/1988, to attain a composition (O<sub>2</sub> concentration having about 0.5 %) of the exhaust gas which corresponds to the air-fuel ratio of A/F = 14.7 where the catalyst can function, it needs much a large quantity of HC. A use of a blow-by gas in this patent document is effective but the blow-by gas has not an amount for efficient to treat an exhaust gas during an operation of an internal combustion engine. It is possible technically to throw the fuel but it results in that the fuel consumption eliminated according to the lean burn system will be lowered.

In Japanese patent laid-open publication No. 97,630/1987, Japanese patent laid-open publication No. 106,826/1987 and Japanese patent laid-open publication No. 117,620/1987, to regenerate a NOx absorbent a flow of an exhaust gas is stopped and the gaseous reducing agent of HC etc. is contacted to NOx absorbent. Further, two NOx absorbents are provided and to flow alternatively the exhaust gas to these two NOx absorbents it is necessary to provide an exhaust gas

change-over mechanism, as a result a structure for the exhaust gas treatment apparatus becomes complicated one.

In WO 93/07363 and WO 93/08383, the exhaust gas is flowed continuously to NOx absorbent and the NOx in the exhaust gas is absorbed during the lean atmosphere and by lowering O<sub>2</sub> concentration in the exhaust gas the absorbed NOx is discharged and NOx absorbent is regenerated. Accordingly, since the change-over of the exhaust gas flow is unnecessary, the problem in the above stated system can dissolved. However, it set forth as a premise of an application of material which absorbs NOx during the lean condition and which can discharge Nox when O<sub>2</sub> concentration in the exhaust gas is lowered.

In case of the above material, since the performance of repeating NOx absorption and discharge causes inevitably a periodic change of a crystal structure of the absorbent, it is necessary to take a careful consideration about a durability of the absorbent.

Further, it is necessary to carry out a treatment for the discharged NOx and in case of a large quantity of the discharged NOx it may cause a post-treatment for the discharged NOx according to the three component catalyst.

#### DISCLOSURE OF INVENTION

In the light of the problems in the above stated prior arts, the present invention is to provide an exhaust gas purification apparatus of an internal combustion engine wherein the purification apparatus having a simple structure of an exhaust gas treatment apparatus, a small consumption amount of the gaseous reducing agents, a superior endurance property and wherein a harm component such as NOx from a lean burn



exhaust gas in the internal combustion engine can be effectively removed and can be converted to a harmless component.

5 Further, the present invention is to provide a catalyst for use in the exhaust gas purification apparatus of an internal combustion engine.

10 According to the present invention, an exhaust gas purification apparatus for use in an internal combustion engine comprises an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub> gas passes and a catalyst so disposed in the exhaust gas duct that it contacts with the exhaust gas.

15 The catalyst chemically adsorbs NO<sub>x</sub> under the condition that a stoichiometric amount of a gaseous oxidizing agent present in the exhaust gas is larger than that of a gaseous reducing agent present in the exhaust gas for reducing NO<sub>x</sub>, while NO<sub>x</sub> being adsorbed is catalytically reduced in the presence of the reducing agent under the condition that the stoichiometric amount  
20 of the oxidizing agent is not larger than that of the reducing agent.

25 According to the present invention, an apparatus for purifying an exhaust gas from an internal combustion engine comprises an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub> gas passes, and a catalyst so disposed in the exhaust gas duct that it contacts with the exhaust gas.

30 The catalyst adsorbs NO<sub>x</sub> under the condition that an amount of a gaseous oxidizing agent present in the exhaust gas is larger than that of a gaseous reducing agent added to the exhaust gas for NO<sub>x</sub> in a stoichiometric relation, while NO<sub>x</sub> being adsorbed is catalytically reduced in the presence of the reducing

agent under the condition that the amount of the oxidizing agent is not larger than that of the reducing agent in the stoichiometric relation.

5 According to the present invention, an apparatus for purifying an exhaust gas from an internal combustion engine comprises an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub> gas passes, and a catalyst so disposed in the exhaust gas duct that it contacts with the exhaust gas.

10 The catalyst adsorbs NO<sub>x</sub> under the condition that a stoichiometric amount of a gaseous oxidizing agent present in a lean combustion exhaust gas is larger than that of a gaseous reducing agent present in the lean combustion exhaust gas for reducing NO<sub>x</sub>, while NO<sub>x</sub> being  
15 adsorbed is catalytically reduced in the presence of the reducing agent under the condition that a stoichiometric amount of the oxidizing agent is not larger than that of the reducing agent in a stoichiometric or fuel rich combustion exhaust gas.

20 According to the present invention, an apparatus for purifying an exhaust gas from an internal combustion engine comprises an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub> gas passes, a device for controlling an air-fuel ratio of  
25 the exhaust gas, and a catalyst so disposed in the exhaust gas duct that it contacts with the exhaust gas.

The air-fuel ratio is switched from the condition that the catalyst chemically adsorbs NO<sub>x</sub> under in the lean combustion exhaust gas to the condition that to the  
30 condition that NO<sub>x</sub> being adsorbed is catalytically reduced in the presence of the reducing agent in a stoichiometric or fuel rich combustion exhaust gas. The catalyst according to the present invention

comprises a heat resistant carrier body and catalytic compounds supported on the carrier body and comprising at least one of sodium and potassium, at least one of magnesium, strontium and calcium, and at least one of platinum, palladium and rhodium.

The catalyst according to the present invention comprises a base member, a heat resistant carrier body supported on the base member and catalytic compounds supported on the carrier body and comprising at least one of sodium and potassium, at least one of magnesium, strontium and calcium, and at least one of platinum, palladium and rhodium.

According to the present invention, the reducing agent to be added to the lean combustion exhaust gas is at least one of gasoline, light oil, kerosene, natural gas, their reformed substances, hydrogen, alcohol, ammonia gas, engine blow-by gas and canister purging gas.

The reducing agent is supplied to the lean combustion exhaust gas in response to signals from the stoichiometric establishing unit.

According to the present invention an exhaust gas purification apparatus further comprises a manifold catalyst disposed in the exhaust gas duct immediately after the engine at the upstream of the catalyst, the catalyst having functions of a three component catalyst and a combustion catalyst.

According to the present invention, in the exhaust gas purification apparatus, a second catalyst is disposed in the exhaust gas duct of a fuel direct injection in-cylinder engine.

According to the present invention, the exhaust gas purification apparatus further comprises a three component catalyst or a combustion catalyst is disposed

in the exhaust gas duct at the upstream of the catalyst.

According to the present invention, an apparatus for purifying an exhaust gas from an internal combustion engine comprising, an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub>, SO<sub>x</sub> and oxygen passes, and a catalyst which chemically adsorbs NO<sub>x</sub> under the condition that the exhaust gas is emitted from lean combustion, and NO<sub>x</sub> being adsorbed is catalytically reduced under the condition that a gaseous reducing agent is added to the lean combustion exhaust gas in such an amount that a stoichiometric amount that a stoichiometric amount of oxygen is not larger than that of the reducing agent.

The catalyst adsorbs or absorbs in the lean condition and releases SO<sub>x</sub> in the stoichiometric or rich condition.

According to the present invention, a catalyst for purifying an exhaust gas from an internal combustion engine which comprises, a base member, a heat resistant carrier body supported on the base member, and catalyst components supported on the carrier body, the carrier body having a number of small hollows extending in the direction of gas flow of the exhaust gas.

According to the present invention, the catalyst compounds comprises at least one of alkali metals, at least one of alkali earth metals other than barium, at least one of noble metals and at least one of rare earth metals.

According to the present invention, an exhaust gas purification apparatus for use in an internal combustion engine comprising, a catalyst for chemically adsorbing NO<sub>x</sub> under a condition where an gaseous oxidizing agent is more than a gaseous reducing agent in a stoichiometric relation between the gaseous oxidizing

agent and the gaseous reducing agent and for catalytic-reducing an adsorbed NOx under a condition where the gaseous reducing agent is equal to or is more than the gaseous oxidizing agent. The catalyst is provided in an exhaust gas flow passage where an exhaust gas generated at a lean air-fuel ratio and at a rich air-fuel ratio or a stoichiometric air-fuel ratio is flowed into.

According to the present invention, an exhaust gas purification apparatus for use in an internal combustion engine comprising a catalyst for chemically adsorbing NOx under a condition where an gaseous oxidizing agent is more than a gaseous reducing agent in a stoichiometric relation between the gaseous oxidizing agent and the gaseous reducing agent and a device which controls an air-fuel ratio to switch conditions between NOx chemical adsorption to the catalyst and catalytic-reduction chemically of NOx to the catalyst.

According to the present invention, an exhaust gas purification apparatus comprises a catalyst which chemically adsorbs NOx under a condition where in a stoichiometric relation between gaseous oxidizing agent and gaseous reducing agent in an exhaust gas flowing an exhaust gas flow passage in the internal combustion engine the gaseous oxidizing agent is more than the gaseous reducing agent and catalytic-reduces an adsorbed NOx under a condition where the gaseous oxidizing agent is equal to or is more than the gaseous reducing agent is provided in the exhaust gas flow passage where an exhaust gas burned at a lean air-fuel ratio and an exhaust gas burned at a rich or stoichiometric air-fuel ratio flow into alternatively.

The exhaust gas purification apparatus according to the present invention comprises a stoichiometric

relation between oxidation and reduction of gaseous oxidizing agent and gaseous reducing agent control means for controlling the stoichiometric relation between gaseous oxidizing agents and gaseous reducing agents comprises a timing establishment means for establishing a timing in which the stoichiometric relation between gaseous oxidizing agent and gaseous reducing agent for changing over from one condition of the gaseous oxidizing agent being more than the gaseous reducing agent to another condition of the gaseous reducing agent being equal to or being more than the gaseous oxidizing agent, and comprises a gaseous reducing agent excess time establishment means for establishing a time which, in the stoichiometric relation between oxidation and reduction, is established under a condition where the gaseous reducing agent is held to being equal to or being more than the gaseous oxidizing agent.

According to the present invention, a catalyst has an ability for catching NOx according to the chemical adsorption and an ability for catalytic-reducing NOx. Even when the oxygen concentration lowers the catalyst does not discharge NOx. These abilities can be obtained by the catalyst which comprises at least one element selected from alkali metals and alkali earth metals in the element periodic table but not including barium (Ba) and at least one selected from noble metals comprising of platinum (Pt), palladium (Pd) and rhodium (Rh). Further, the catalyst has an ability for catalytic-oxidizing HC or CO etc..

The catalyst has a high NOx absorption ability under the lean atmosphere and further under the catalyst temperature of 250-500 °C. Further, to recover NOx adsorbing ability in accordance with the reduction of

the absorbed NO<sub>x</sub>, it is seen that the catalyst must maintain a time of about 30 seconds or less than 30 seconds under the stoichiometric atmosphere or the rich atmosphere.

5       Accordingly, to perform effectively NO<sub>x</sub> adsorption and to recover NO<sub>x</sub> adsorbing ability, it is desirable to provide the catalyst at a position of an exhaust gas duct where an inlet port gas temperature of the catalyst is 250-500 °C. The above temperature range is one which  
10       can obtain normally under the car-body floor.

      NO<sub>x</sub> adsorbing ability of the catalyst is lowered because that the catalyst suffers from poisoning by SO<sub>x</sub> originated fuel (gasoline). It is seen that, when the catalyst which suffered from poisoning by SO<sub>x</sub> is  
15       maintained several minutes or ten (10) minutes at 400-800 °C under the stoichiometric atmosphere or the rich atmosphere, SO<sub>x</sub> is removed and then NO<sub>x</sub> adsorbing ability is recovered.

      Accordingly, under the condition where the gasoline  
20       quality is bad (high sulfur content) and the catalyst suffers from poisoning by SO<sub>x</sub>, it is desirable to provide the catalyst at a position of an exhaust gas duct where an inlet port gas temperature of the catalyst is 400-800 °C. The above temperature range is one which  
25       can obtain under the car-body floor.

      In case where the catalyst is used as the catalyst for an automobile, it is desirable to form the honeycomb catalyst having NO<sub>x</sub> adsorption ability of more than 0.01 mol per an apparent honeycomb volume one (1) liter.

30       Further, it is desirable to set the specific surface area of the catalyst layer on the honeycomb substrate (the honeycomb base body) measured by absorbing nitrogen

according to BET method being more than 50 m<sup>2</sup>/g.

In the exhaust gas, the gaseous oxidizing agents are O<sub>2</sub>, NO, NO<sub>2</sub>, etc. and are mainly oxygen. The gaseous reducing agents are HC supplied in an internal combustion engine, HC (including oxygen containing hydrocarbon) generated in a combusting process as a derivative from fuel, CO, H<sub>2</sub>, etc. and further a reducing material of such as HC which is added in the exhaust gas as a reducing component.

When the lean exhaust gas is contacted with the three component catalyst, HC, CO, H<sub>2</sub>, etc. as the gaseous reducing agents for reducing NO<sub>x</sub> to nitrogen (N<sub>2</sub>) cause a combustion reaction with oxygen (O<sub>2</sub>) as the gaseous oxidizing agent in the exhaust gas. And NO<sub>x</sub> (NO and NO<sub>2</sub>) reacts with these gaseous reducing agents and is reduced to nitrogen (N<sub>2</sub>). In normally, since both reactions proceed in parallel, a utilization rate of the gaseous reducing agents for reducing NO<sub>x</sub> is low.

In particularly, at a high temperature more than 500 °C of a reaction temperature (it depends on a catalyst material), an occupation rate of the latter reaction becomes large. Hence, by separating NO<sub>x</sub> from the exhaust gas using the catalyst (at least it separates from O<sub>2</sub> in the exhaust gas) and after that by carrying out the catalytic-reaction with the gaseous reducing agents it is possible to carry out effectively the reduction of NO<sub>x</sub> to N<sub>2</sub>. According to the present invention, using the catalyst NO<sub>x</sub> in the lean exhaust gas is adsorption-removed, NO<sub>x</sub> in the exhaust gas is separated from O<sub>2</sub>.

Next, according to the present invention, with regard to the oxidation reduction relation, namely the stoichiometric relation between oxidation and reduction,

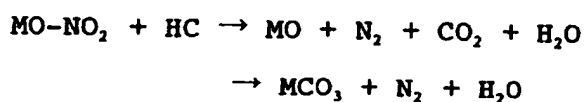


which is constituted by the gaseous oxidizing agents ( $O_2$  and  $NO_x$  etc.) and the gaseous reducing agents ( $HC$ ,  $CO$ ,  $H_2$  etc.) in the exhaust gas, the condition where the gaseous reducing agent is equal to or is larger than the gaseous oxidizing agent is made and  $NO_x$  absorbed on the catalyst is reduced to  $N_2$  according to the catalytic-reaction with the gaseous reducing agent such as  $HC$ .

$NO_x$  in the exhaust gas is substantially constituted of  $NO$  and  $NO_2$ . The reaction property  $NO_2$  is rich in comparison with that of  $NO$ . Accordingly, when  $NO$  is oxidized to  $NO_2$ , the adsorption-removal and the reduction of  $NO_x$  in the exhaust gas are performed easily.

The present invention includes a method of oxidizing  $NO_x$  in the exhaust gas to  $NO_2$  by the coexistent  $O_2$  and then remove, and an oxidation means for attaining the above method such as the means having  $NO$  oxidation function and the means for providing an oxidation catalyst at a pre-stage of the catalyst.

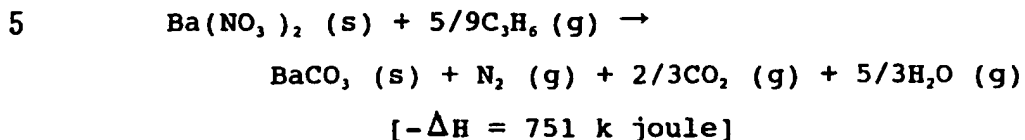
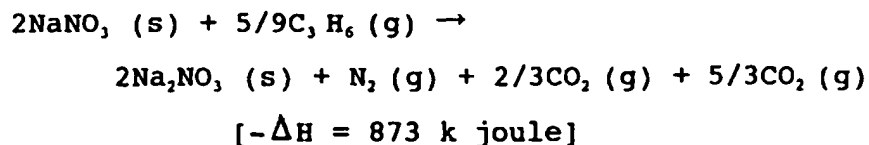
The reduction reaction of a chemically adsorbed  $NO_2$  according to the present invention will be described generally with following reaction formulas.



Herein,  $M$  indicates a metal element and  $MO-NO_2$  indicates a combination state of  $NO_2$  of a metal oxide surface. A reason for employing  $MCO_3$  as the reduction generation substance will be explained in a latter stated portion.

The above reaction is an exothermic reaction. As the metal  $M$ , alkali metals and alkali earth metals are taken up, and by representing  $Na$  and  $Ba$  respectively the reaction heat is estimated. It becomes as following

under a standard condition (1 atmosphere, 25 °C).



Herein, s indicates a solid state and g indicated a gaseous state.

10 Here, a thermodynamical value of the solid state is used as that of an adsorbed state.

Incidentally, the combustion heat of  $\text{C}_3\text{H}_8$ , 5/9 mole is 1,070 k joule and each of the above reactions is exothermic heat being a match for the combustion heat of HC.

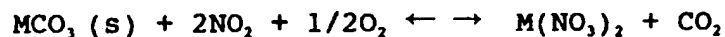
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As a matter of course, this exothermic heat is transferred to the exhaust gas and then a local raise in temperature of a surface of the catalyst can be restrained.

20 In case that catching agent for NOx is NOx absorbent, since NOx which is picked up in a bulk of the absorbent is reduced, there is a limitation for heat transfer to the exhaust gas, accordingly a raise in temperature of the absorbent causes. This exothermic heat shifts

25 balance of the absorption reaction to a side of NOx discharging or NOx emission.

absorption  $\rightarrow$



$\leftarrow$  discharging

30 Even though the concentration of the gaseous reducing agents is heightened to reduce rapidly NOx concentration

in the exhaust gas which is discharged to an outside of the absorbent, the reaction between NO<sub>2</sub> and HC in the gaseous phase does not proceed.

5 Accordingly, the discharging amount of NO<sub>x</sub> can not reduce fully by an increment of the gaseous reducing agents. Further, at a stage where the adsorption amount of NO<sub>x</sub> is small, a reduction operation may carry out, however since the regeneration frequency of NO<sub>x</sub> absorbent increases, it is not put in a practical use.

10 The catalyst according to the present invention generates a small absolute amount exothermic heat so as to catch NO<sub>x</sub> at a vicinity of the surface thereof in accordance with the chemical adsorption and also the arise in temperature of the catalyst is small so as to transfer the heat rapidly to the exhaust gas.  
15 Accordingly, it is possible to prevent the discharging of the once caught NO<sub>x</sub>.

20 The catalyst according to the present invention is characterized to the material which catches NO<sub>x</sub> at the surface thereof in accordance with the chemical adsorption and the material which does not cause NO<sub>x</sub> discharging or NO<sub>x</sub> emission in accordance with the exothermic reaction during the reduction of NO<sub>x</sub>.

25 Further, the catalyst according to the present invention is characterized to the material which catches NO<sub>x</sub> at the surface thereof in accordance with the chemical adsorption or at a vicinity of the surface thereof in accordance with a chemical combination and the material which does not cause NO<sub>x</sub> discharging in  
30 accordance with the exothermic reaction during the reduction of NO<sub>x</sub>.

Further, the catalyst according to the present invention is characterized to catch NO<sub>x</sub> contained in the

lean exhaust gas at the surface thereof in accordance with the chemical adsorption and during the reduction of NO<sub>x</sub> this catalyst is a material which does not cause NO<sub>x</sub> discharging in accordance with the lowering of the oxygen concentration.

The inventors of the present invention found out that the above stated characterizations can realize using a catalyst which is selected from at least one of alkali metals and alkali earth metals classified in an element periodic table and at least one of noble metals selected from platinum (Pt), rhodium (Rh) and palladium (Pd) but does not contain barium (Ba). Preferably, the catalyst according to the present invention includes at least one kind element selected from potassium (K), sodium (Na), and strontium (Sr), and noble metal elements.

The exhaust gas purification apparatus according to the present invention arranges at an exhaust gas flow passage the catalyst including at least one kind element selected from potassium (K), sodium (Na), magnesium (Mg), strontium (Sr) and calcium (Ca) and noble metal elements.

In the exhaust gas purification apparatus, in the stoichiometric relation between oxidation and reduction of each of the components included in the exhaust gas, it forms the condition where the gaseous oxidizing agent is equal to or is more than the gaseous reducing agent and NO<sub>x</sub> is chemically adsorbed on the catalyst, next it forms the condition where the gaseous reducing agent is equal to or is more than the gaseous oxidizing agent, thereby NO<sub>x</sub> absorbed on the catalyst is reduced according to the catalytic-reaction with the gaseous reducing agent to harmless N<sub>2</sub>.

The catalyst in the present invention can be applied suitably in particular by following substances.

The composition is constituted of a metal and a metal oxide substance (or a complex oxide substance) which contains at least one selected from potassium (K), sodium (Na), magnesium (Mg), strontium (Sr) and calcium (Ca), at least one selected from rare earth metals, and at least one of elements selected from noble metals including platinum (Pt), rhodium (Rh), and palladium (Pd). This composition is one which these elements are supported on a porous heat-withstanding metal oxide substance. This composition has a superior NO<sub>x</sub> adsorbing ability.

As the earth metal element, cerium (Ce) or lanthanum (La) is preferable, in particularly Ce is preferable. The earth metal element has a function for exhibiting the three component function to the catalyst under the stoichiometric atmosphere or the rich atmosphere.

At least one of titanium (Ti) and silicon (Si) can be added to the catalyst according to the present invention. Accordingly, the heat resistant property and SO<sub>x</sub> endurance property of the catalyst can be improved. Ti or Si has a function for adsorbing or absorbing SO<sub>x</sub> under the lean atmosphere or for discharging the adsorbed SO<sub>x</sub> or the absorbed SO<sub>x</sub> under the stoichiometric atmosphere or the rich atmosphere.

In the catalyst of the present invention, alkali metals, alkali earth metals, noble metals, rare earth elements, titanium (Ti) and silicon (Si) are held on the porous support or the porous carrier member and the porous support or the porous carrier member supported or carried on a substance body. As the porous support, from an aspect of the heat resistant property or the heat resistant ability,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be preferably employed. As the substance body, a cordierite, mullite,

a metal, for example, a stainless steel can be preferably employed.

As the crystal structure of Ti which is held on the porous support, an amorphous oxide state is preferable.  
5 Further, in case where the catalyst includes Si and alkali earth metals at the same time, as both the crystal structures Si and alkali earth metals, an amorphous oxide state is preferable.

In the catalyst of the present invention, to the  
10 porous support (porous carrier member) of 100 wt% it is preferable to include alkali metals of 5-20 wt%, and to the porous support of 100 wt% it is preferable to include alkali earth metals of 3-40 wt%. Further, to the porous support of 100 wt%, it is preferable to  
15 include Pt of 0.5-3 wt%, Rh of 0.05-0.3 wt%, and Pd of 0.5-15 wt%, respectively. Mg has a function for preventing the cohesion or the condensation of the active components which are held on the porous support, such as the noble metal.

20 To the porous support of 100 wt%, it is preferable to include the rare earth metals of 5-30 wt%. To the porous support of 100 wt%, it is preferable to include Ti of 0.1-30 wt%, and to the porous support of 100 wt%, it is preferable to include Si of 0.6-5 wt% as silica.

25 The present invention provides the catalyst which comprises of, on the porous support, sodium (Na), magnesium (Mg), and at least one element selected from platinum (Pt), palladium (Pd), and rhodium (Rh), and at least one selected from cerium (Ce) and lanthanum (La)  
30 are held, and further to the porous support of 100 wt%, Na of 5-20 wt%, Mg of 1-40 wt% under a weight ratio  $Mg/(Na + Mg)$ , Pt of 0.5-3 wt%, Rh of 0.05-0.3 wt%, and Pd of 0.5-15 wt% are included.

In the exhaust gas purification apparatus according to the present invention, to chemically adsorb NO<sub>x</sub> to the catalyst or catalytic-reduce the chemically adsorbed NO<sub>x</sub>, it requires the means for controlling the stoichiometric relation between oxidation and reduction by the gaseous oxidizing agents and the gaseous reducing agents in the exhaust gas. By the provision of the stoichiometric relation between oxidation and reduction control means, it can carry out the operation for forming the condition where the gaseous reducing agent is equal to or is more than the gaseous oxidizing agent, namely, for example, the combustion condition in the internal combustion engine is made to the stoichiometric air-fuel ratio or to the fuel excess (the rich), or the gaseous reducing agent is added to the lean burn exhaust gas.

The former can be attained by a following method.

A method is one the fuel injection amount is controlled in accordance with the output of the oxygen concentration sensor and the output of the intake air flow amount sensor provided in the exhaust gas duct. In this method, a part of the plural cylinders is made under the fuel excess and the remainder thereof is made under the fuel shortage, and the components of the mixture exhaust gas from the whole cylinders form the condition where the gaseous reducing agent is equal to or is more than the gaseous oxidizing agent in the stoichiometric relation between the oxidation and the reduction.

The latter can be attained by each of following methods.

A method is one the gaseous reducing agent is thrown at the upstream of the catalyst in the exhaust gas flow.

As the gaseous reducing agent, gasoline, light gas oil, natural gas, reforming material thoseof, hydrogen, alcohol materials and ammonium materials can be applied. It is effective to introduce the blow-by gas and the  
5 canister purging gas at the upstream of the catalyst and to throw the gaseous reducing agent such as hydrocarbon (HC) contained in the above materials. In the fuel direct injection system internal combustion engine, it is effective to inject the fuel during the exhausting  
10 process and to throw the fuel as the gaseous reducing agent.

As the catalyst in the present invention, the various kinds of shapes can be applied. In addition to the honeycomb shape which is obtained by coating the  
15 catalyst components to the honeycomb shape structure member comprised of cordierite or metal materials such as a stainless steel, the pellet shape, the plate shape, the particle shape and the powder shape can be applied.

In the present invention, the apparatus can provide  
20 the means for establishing the timing where the gaseous reducing agent is equal to or is more than the gaseous oxidizing agent. The above timing is obtained by each of following methods.

The timing is one in accordance with the air-fuel  
25 ratio setting signal which is determined by ECU (engine control unit), the engine rotation number signal, the inhale air amount signal, the intake air pipe pressure signal, the speed signal, the throttle valve opening degree signal, the exhaust temperature etc., NOx  
30 discharging amount during the lean operation time is estimated and the integration value thereof is exceeds over a predetermined setting value.

The timing is one, in accordance with the signal of



the oxygen sensor (or A/F sensor) arranged at the upstream or the downstream of the catalyst in the exhaust gas flow passage, the accumulated oxygen amount is detected, and the accumulated oxygen amount exceeds over a predetermined amount. As a modified embodiment, the accumulated oxygen amount during the lean operation time exceeds over a predetermined amount.

The timing is one, in accordance with the signal of NOx sensor arranged at the upstream of the catalyst in the exhaust gas flow passage, the accumulated NOx amount is detected, and the accumulated NOx amount during the lean operation time exceeds over a predetermined amount.

The timing is one, in accordance with the signal of NOx sensor arranged at the downstream of the catalyst in the exhaust gas flow passage, NOx concentration is detected, and NOx concentration exceeds over a predetermined concentration.

According to the present invention, further the apparatus provides the means for establishing the maintenance time where the gaseous reducing agent is equal to or is more than the gaseous oxidizing agent. The maintain time of the gaseous reducing agent excess condition and the throw-in gaseous reducing agent amount can be determined taking into the consideration of the specifications and the characteristics of the adsorbent and the internal combustion engine. The above methods can be realized by adjusting the stroke, the injection time and the injection interval of the fuel injector.

#### BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a constructive view showing a representative embodiment of an exhaust gas purification apparatus for use in an internal combustion engine

according to the present invention;

Fig. 2 is a time lapse characteristic of NOx purification rate where a rich operation and a lean operation are repeated alternatively in accordance with a method for purifying an exhaust gas of an internal combustion engine according to the present invention;

Fig. 3 is a relationship between NOx concentration and NOx purification rate in a lean exhaust gas;

Fig. 4 is NOx purification rate in a stoichiometric exhaust gas;

Fig. 5A and 5B are relationships between an inlet port NOx purification rate and an outlet port NOx purification rate of a catalyst in case where a rich (stoichiometric) operation is changed over to a lean operation;

Fig. 6A and 6B are relationships between an inlet port NOx purification rate and an outlet port NOx purification rate of a catalyst in case where a rich (stoichiometric) operation is changed over to a lean operation;

Fig. 7 is a block diagram showing a method for controlling an air-fuel ratio

Fig. 8 is a flow chart showing a method for controlling an air-fuel ratio;;

Fig. 9 is a flow chart showing a method for accumulating NOx discharging amount during a lean operation;

Fig. 10 is a flow chart showing NOx amount assumption in the flow chart shown in Fig. 8;

Fig. 11 is a flow chart showing NOx amount assumption in the flow chart shown in Fig. 8;

Fig. 12 is a flow chart showing NOx amount assumption in the flow chart shown in Fig. 8;

Fig. 13 is a flow chart showing NOx amount assumption in the flow chart shown in Fig. 8;

Fig. 14 is a constructive view showing an embodiment of an exhaust gas purification apparatus on which a manifold catalyst is provided;

Fig. 15 is a constructive view showing an embodiment of an exhaust gas purification apparatus in a fuel direct injection in-cylinder engine;

Fig. 16 is a constructive view showing an embodiment of an exhaust gas purification apparatus on which a post-catalyst is provided;

Fig. 17 is a constructive view showing an embodiment of an exhaust gas purification apparatus in which a gaseous reducing agent is added to an upstream of a catalyst;

Fig. 18A, 18B and 18C are views showing NOx purification characteristic where a mode operation is carried out;

Fig. 19 is a graph showing NOx purification characteristic where an oxygen concentration is varied using a model gas;

Fig. 20 is a graph showing NOx purification characteristic where an oxygen concentration is varied using a model gas;

Fig. 21 is a view showing NOx purification rate for optimizing Na supported amount;

Fig. 22 is a view showing NOx purification rate for optimizing Mg supported amount;

Fig. 23 is a view showing NOx purification rate for optimizing Ce supported amount;

Fig. 24 is a view showing NOx purification rate for optimizing Rh and Pt supported amount;

Fig. 25 is a view showing NOx purification rate for

optimizing Pd and Pt supported amount; and

Fig. 26 is a view showing NOx purification rate for optimizing Sr supported amount.

## 5 BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, one embodiment of an exhaust gas purification apparatus and an exhaust gas purification catalyst for use in an internal combustion engine according to the present invention will be explained.

10 However, the present invention will not be limited within following embodiments.

### Characteristics and Representative Embodiments of Catalyst

15 The characteristics of a catalyst for use in an internal combustion engine in accordance with a method according to the present invention will be explained. (Catalyst Preparation Method)

20 A catalyst N-N9 was obtained according to a following method.

Nitric acid alumina slurry was obtained by mixing alumina powders with alumina-sol obtained by peptizing boehmite by nitric acid. After a cordierite honeycomb was immersed in the slurry and the cordierite honeycomb was pulled up rapidly. The slurry enclosed in a cell was removed by performing an air-blow process, after the drying of the honeycomb the honeycomb was calcined at 450 °C.

25 The above processes was carried out repeatedly and the alumina of 150 g per 1 (one) litter of an apparent volume of the honeycomb was coated.

30 On this alumina coated honeycomb catalyst active components were held and then a honeycomb shape catalyst

was obtained.

In concretely, the alumina coated honeycomb was immersed in cerium nitrate ( $\text{Ce}(\text{NO}_3)_3$ ) solution and the honeycomb was dried at 200 °C and after the drying the honeycomb was calcined for 1 (one) hour at 600 °C. In  
5 succession, it is immersed in a mixture liquid comprised of sodium nitrate ( $\text{NaNO}_3$ ) solution, titania-sol solution and magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) solution, after the honeycomb was dried at 200 °C the honeycomb was calcined  
10 for 1 (one) hour at 600 °C.

Further, the honeycomb was immersed in a mixture solution comprised of dinitrodiamine Pt nitrate solution and rhodium nitrate ( $\text{Rh}(\text{NO}_3)_3$ ) solution, and then after the honeycomb was dried at 200 °C the honeycomb was  
15 calcined for 1 (one) hour at 450 °C. In finally, it is immersed in magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) solution and after the honeycomb was dried at 200 °C the honeycomb was calcined for 1 (one) hour at 450 °C.

With the above process, the honeycomb shape catalyst was obtained, this catalyst was one where Ce, Mg, Na, Ti, Rh and Pt were held on alumina ( $\text{Al}_2\text{O}_3$ ) and is 2Mg -  
20 (0.2Rh, 2.7Pt) - (18Na, 4Ti, 2Mg) - 27Ce/ $\text{Al}_2\text{O}_3$ . Herein, / $\text{Al}_2\text{O}_3$  shows that the active component was held on  $\text{Al}_2\text{O}_3$ , a numerical value before the element is weight (g) of an indicated metal component which was supported per 1  
25 (one) litter of the apparent volume of the honeycomb.

An expressed order shows a support order or a carrier order and the elements were held in accordance with an order of the component for separating from the expressed  
30 component near to  $\text{Al}_2\text{O}_3$ , namely, on  $\text{Al}_2\text{O}_3$ , 27Ce, (18Na, 4Ti, 2Mg), (0.2Rh, 2.7Pt), and 2Mg are held in sequence,

and the component bound up with parenthesis were supported at the same time. Incidentally, a support amount of the respective of the active components was enable varied by varying the active component concentration in the immersed solution.

A catalyst N-K9 was prepared according to a following method.

In place of sodium nitrate ( $\text{NaNO}_3$ ) solution used in the preparation for the catalyst N-N9, potassium nitrate ( $\text{KNO}_3$ ) solution was used and others were a similar method for preparing the catalyst N-N9. As a result, the catalyst N-K9 comprised of 2Mg - (0.2Rh, 2.7Pt) - (18K, 4Ti, 2Mg) - 27Ce/ $\text{Al}_2\text{O}_3$ , was obtained.

Further, with a similar method, a comparison catalyst N-R2 comprised of 2Mg - (0.2Rh, 2.7Pt) - 27Ce/ $\text{Al}_2\text{O}_3$ , was obtained.

(Performance Evaluation Method)

After the catalysts obtained by the above stated methods were thermally treated at 700 °C under an oxidizing atmosphere for 5 (five) hours, the characteristics were evaluated using following methods.

On an automobile in which a lean burn gasoline engine was mounted having the displacement volume of 1.8 liters, the honeycomb shape catalysts having a volume of 1.7 liters prepared using the above stated methods were mounted and then NOx purification characteristics were evaluated.

(Characteristics of Catalysts)

The catalyst N-N9 was mounted and a 30 seconds period of a rich operation having A/F = 13.3 and an about 20 minutes period of a lean operation having A/F = 22 were repeated alternatively and then NOx purification characteristics shown in Fig. 2 were obtained.

In case where the fuel is the gasoline, a mass composition of the gasoline comprises carbon (C) of about 85.7 % and hydrogen (H) of about 14.3 %. Herein, when the gasoline of F (g) is burned, carbon (C) of  
5 0.857 x F (g) reacts with oxygen (O<sub>2</sub>) of 0.857F/12 mol and hydrogen (H) of 0.143 x F (g) reacts with oxygen (O<sub>2</sub>) of 0.143F/4 mol. A necessary air amount A (g) is expressed as following:

10 
$$A = ((0.857/12 + 0.143/4)F \times 28.8) / 0.21 = 14.7F$$
 herein, 28.8 is air molecular amount (g/mol) and 0.21 is oxygen (O<sub>2</sub>) amount rate in air.

A/F = 14.7 indicates a stoichiometric air-fuel ratio.

Accordingly, under A/F = 13.3, to the fuel (a gaseous reducing agent) of F (g), it shows an insufficient  
15 condition (a reduction atmosphere) of the air (the gaseous oxidizing agent) of 1.39F (g). On the other hand in case of A/F = 22, to the fuel of F (g), it shows an excess condition (an oxidization atmosphere) of the air (the gaseous oxidizing agent) of 7.31F (g).

20 From understood in this figure (Fig. 2), NO<sub>x</sub> during the lean operation time was purified in accordance with this catalyst.

NO<sub>x</sub> purification rate during the lean operation time was decreased gradually and the purification rate having  
25 100 % at an initial period became about 40 % after 20 minutes. However, the lowered purification rate was recovered to 100 % under 30 seconds period of the rich operation. When the lean operation was carried out again NO<sub>x</sub> purification performance was recovered and the  
30 above stated change in time lapse was repeated.

Even when the lean operation and the rich operation were repeated in plural times, the velocity of the lowering in time lapse of NO<sub>x</sub> purification rate during

the lean operation was unchanging, this shows that NOx absorption performance was fully regenerated according to the rich operation.

5 The vehicle speed was about 40 km/h constant (the exhaust gas space velocity (SV) was about 20,000/h constant) and NOx concentration in the exhaust gas was varied by varying the ignition periods and the relationship between NOx concentration and NOx purification rate in the lean exhaust gas was determined and then Fig. 3 was obtained.

10 NOx purification rate was lowered in lapse of time, however more NOx concentration lowered more the lowering speed was small. Until to reach NOx purification rates 50% and 30%, the catching NOx amount was estimated through Fig. 3 and was as shown in Table 1.

Table 1

NOx concentration in inlet port exhaust gas (ppm)	NOx amount purified until purification rate 50% (mol)	NOx amount purified until purification rate 30% (mol)
about 50	0.030	0.041
about 120	0.031	0.047
about 230	0.030	0.045
about 450	0.030	0.042
about 550	0.026	0.038

20 NOx catching amounts were substantially constant in regardless of NOx concentration. The absorption amount did not depend to the concentration (the pressure) of the adsorbent and this is a feature of the chemical adsorption.

25 In the test catalysts, first of all there were Pt



particles as NO<sub>x</sub> absorption medium. A result of CO  
adsorption amount evaluation which is frequently used as  
means for evaluating the exposed Pt amount was carried  
out, and CO adsorption amount (at 100 °C) was  $4.5 \times 10^{-4}$   
5 mol. This value was about 1/100 of the above stated NO  
adsorption amount and therefore it was clear that Pt  
does not work as a main role for NO<sub>x</sub> adsorbent.

On the other hand, BET surface area (measured by  
nitrogen adsorption) of this catalyst (including  
10 cordierite as a substrate) was measured about 25 m<sup>2</sup>/g and  
was 28,050 m<sup>2</sup> per the honeycomb 1.7 liters. Further,  
the chemical structure about Na of the catalyst  
according to the present invention was studied. From  
the facts that CO<sub>2</sub> gas was generated and dissolved in an  
15 inorganic acid and from a value of a point of inflection  
in a pH neutralization titration curve line, it was  
judged Na existed mainly as Na<sub>2</sub>CO<sub>3</sub>.

Supposing all of the surface was occupied by Na<sub>2</sub>CO<sub>3</sub>,  
Na<sub>2</sub>CO<sub>3</sub> of 0.275 mol would be exposed on the surface. (As  
20 the specific gravity of Na<sub>2</sub>CO<sub>3</sub> is 2.533 g/mol, the volume  
of one molecular of Na<sub>2</sub>CO<sub>3</sub> can be estimated. Supposing  
Na<sub>2</sub>CO<sub>3</sub> is a cube, an area of one face of Na<sub>2</sub>CO<sub>3</sub> was  
estimated and the estimated area was used as the  
occupation area of the surface Na<sub>2</sub>CO<sub>3</sub> ).

25 In accordance with the above stated reaction formula,  
Na<sub>2</sub>CO<sub>3</sub> of 2.75 mol has an ability for adsorbing NO<sub>2</sub> of  
0.55 mol. However, NO<sub>x</sub> amount which had been removed by  
the catalyst according to the present invention has an  
order of 0.04 mol which is less than 1/10 of the ability.

30 The above difference attributed the cause that BET  
method evaluated the physical surface area and the  
surface area of Al<sub>2</sub>O<sub>3</sub> with the surface area of Na<sub>2</sub>CO<sub>3</sub> was  
evaluated.

The above stated evaluations show the adsorbed NOx amount was far and way NOx catching power of Na<sub>2</sub>CO<sub>3</sub> bulk and at least NOx was caught at a limited area of the surface or the vicinity of the surface of Na<sub>2</sub>CO<sub>3</sub>.

5 Further, in Fig. 3, the velocity of the lowering in the purification rate lowered at about NOx purification rate of 20%, however this shows that the reducing reaction caused according to the catalyst function.

10 Fig. 4 shows NOx purification rate of the immediately after time where the lean operation has changed over to the stoichiometric operation.

Fig. 5A and 5B show NOx purification characteristic of the time where the lean operation has changed over to the stoichiometric operation, and Fig. 6A and 6B show  
15 NOx purification characteristic of the time where the lean operation has changed over to the rich operation.

Fig. 5A and 5B shows NOx concentrations of an inlet port and an outlet port of the catalyst N-N9, Fig. 5A shows case the air-fuel ratio is changed over from the  
20 lean condition having A/F = 22 to the rich condition having A/F = 14.2.

Herein, under A/F = 14.2, to the fuel of F (g), it shows a condition of a shortage of the air (the gaseous oxidizing agent) of 0.5 F (g), namely the reduction  
25 atmosphere.

In the start time of the regeneration at the immediately after time of the rich change-over, since the exhaust gas NOx concentration in the exhaust gas of A/F = 14.2 is high, the inlet port NOx concentration in  
30 the rich operation increases largely and in company with this the outlet NOx concentration increases transient. However, the outlet port NOx concentration lowers largely always the inlet port NOx concentration. The

regeneration proceeds rapidly and the outlet port NOx concentration reaches to a vicinity of zero (0) with a short time.

Fig. 5B shows case where the air-fuel ratio is changed over from the lean condition having  $A/F = 22$  to the rich condition having  $A/F = 14.2$ . Similarly to Fig. 5A, the outlet port NOx concentration lowers largely always to the inlet port NOx concentration and further the outlet port NOx concentration reaches to a vicinity of zero (0) with a shorter time.

As clearly understood from the above, an  $A/F$  value as the regeneration condition gives an influence to the time for requiring the regeneration.  $A/F$  value, the time and gaseous reducing agent amount suitable for the regeneration are influenced by the composition, such as the shape, the temperature and SV value of the catalyst, the kind of the gaseous reducing agent, and the shape and the length of the exhaust gas flow passage. Accordingly, the regeneration condition is determined overall under the consideration of the above stated these items.

Fig. 6A and 6B show NOx concentrations of an inlet port and an outlet port of the catalyst N-K9. Fig. 6A shows case the air-fuel ratio is changed over from the lean condition having  $A/F = 22$  to the rich condition having  $A/F = 14.2$ , and Fig. 6B shows case the air-fuel ratio is changed over from the lean condition having  $A/F = 22$  to the rich condition having  $A/F = 14.2$ .

Similarly to case of the above catalyst N-N9, the outlet port NOx concentration lowers largely always the inlet port NOx concentration and further the regeneration of the catalyst proceeds with a short time. (Basic Characteristics of Catalyst)

Using a model gas, the basic characteristics, in particular an affect for giving NOx purification rate by the oxygen concentration, were evaluated.

5 The cordierite honeycomb of the catalyst N-N9 having 6 ml was filled up in a silica reaction tube having an inner diameter of 28 mm and the model gas was passed through the tube. The oxygen concentration in the model gas was varied and an affect for giving to NOx purification rate by the oxygen concentration was  
10 studied. The reaction temperature was 300°C at the inlet port gas temperature of the catalyst.

At first, the gas composition comprises of O<sub>2</sub> of 5 % (a volume ratio: same hereinafter), NO of 600 ppm, C<sub>3</sub>H<sub>6</sub> of 500 ppm (1,500 ppm as C<sub>1</sub>), CO of 1,000 ppm, CO<sub>2</sub> of  
15 10 %, H<sub>2</sub>O of 10 %, and the balance of N<sub>2</sub> was passed through. After ten (10) minutes where NOx purification rate has been stable, only the oxygen concentration was lowered to a predetermined value and maintained for twenty (20) minutes, finally the gas composition was  
20 returned again at the initial time gas composition. NOx concentration change for the above time interval was varied with six kinds of O<sub>2</sub> concentration, which were 0 %, 0.5 %, 0.7 %, 1 %, 2 % and 3 %, and the graphs shown in Fig. 19 was obtained.

25 In Fig. 19, in case where the oxygen concentration in the lean gas was lowered, namely in case where the oxidization atmosphere became weak and the reduction atmosphere became strong, it was admitted that there had a tendency that NOx purification rate was heightened.  
30 And this suggests that this catalyst purifies NOx according to the reduction.

Further, in Fig. 19, NOx purification rate was a positive value at all times and in accordance with this

catalyst NOx concentration passed through the catalyst did not increase in regardless of the oxygen concentration.

5       Next, the gas composition comprises of O<sub>2</sub> of 5 %, NO of 600 ppm, and the balance of N<sub>2</sub> was passed through and the oxygen concentration in this gas was similarly varied and Fig. 20 was obtained. In this examination, it was a feature where the gaseous reducing agent was not included in the gas. In Fig. 20, by lowering the  
10       oxygen concentration and even the oxidization atmosphere was weakened, then NOx purification rate did not improve. This suggests that this catalyst purifies NOx according to the reduction.

15       In Fig. 20, NOx purification rate had not a positive value, and further in this catalyst according to the oxidization atmosphere once caught NOx is not discharged or not emitted.

#### An Exhaust Gas Purification Apparatus

20       Fig. 1 is a whole construction of an apparatus showing one embodiment of an exhaust gas purification apparatus according to the present invention.

25       An exhaust gas purification apparatus according to the present invention comprises an air intake system having an engine 99 for enable to carry out the lean burn operation, an air flow sensor 2, a throttle valve 3 etc., an exhaust system having an oxygen concentration sensor 19 (or A/F sensor), an exhaust gas temperature sensor 17 and a catalyst 18 etc., and an engine control  
30       unit (ECU) etc..

ECU comprises I/O LSI as an input/output interface, an execution processing unit MPU, memory apparatuses RAM and ROM for storing many control programming, and a

timer counter, etc..

The above stated exhaust gas purification apparatus functions as following. After the inhale air to the engine 99 is filtered through an air cleaner 1, the inhale air is metered according to the air flow sensor 2. Further, the air passes through the throttle valve 3 and is received the fuel injection through an injector 5 and after is supplied to the engine 99 as an air-fuel mixture. The signals of the air flow sensor 2 and the other signals are inputted into ECU (engine control unit).

In ECU, by latter stated method the operation conditions of the internal combustion engine and the conditions of the catalyst are evaluated and an air-fuel ratio is determined. By controlling the injection period etc. of the injector 5, the fuel concentration of the air-fuel mixture is established at a predetermined value.

The air-fuel mixture sucked in the cylinders is ignited and burned through an ignition plug 6 which is controlled according to the signals from ECU. The combustion exhaust gas is led to an exhaust gas purification system. A catalyst 18 is provided in the exhaust gas purification system, during the stoichiometric operation NOx, HC and CO are purified according to the three component catalyst function and during the lean operation time NOx is purified according to NOx adsorbing ability and at the same time HC and CO are purified according to the combusting function.

Further, in accordance with the judgment and the control signal of ECU, at the lean operation time NOx purification ability of a catalyst 18 is judged always and in case where NOx purification ability lowers the

air-fuel ratio etc. is shifted to the rich side and then NOx purifying ability is recovered. With the above stated operations, in this apparatus, the exhaust gas under all engine combustion conditions including the lean operation and the stoichiometric operation (including rich operation) is purified effectively.

The fuel concentration (hereinafter, the air-fuel ratio) of the air-fuel mixture supplied to the engine is controlled as followings. Fig. 7 is a block diagram view showing the air-fuel ratio control method.

From a load sensor output for outputting a signal in response to a step-in amount of an acceleration pedal, an output signal of the intake air amount metered by the air flow sensor 2, an engine rotation number signal detected by a crank angle sensor, a throttle sensor signal for detecting the throttle valve opening degree, an engine water coolant temperature signal, a startor signal etc., ECU 25 determines the air-fuel ratio (A/F) and this signal is compensated according to a signal which is feed-backed from the oxygen sensor.

In cases of a low temperature time, an idling time and a high load time etc., the above feed-back control is stopped according to the signal of the respective sensor and the respective switching means. Further, since the apparatus has an air-fuel ratio compensation leaning function. With this air-fuel ratio compensation leaning function the apparatus can correspond accurately the delicate change and the abrupt change of the air-fuel ratio.

In case where the determined air-fuel ratio is the stoichiometric condition ( $A/F = 14.7$ ) and the rich condition ( $A/F < 14.7$ ), by the indication of ECU the injection conditions for the injector 5 are determined

and thereby the stoichiometric operation and the rich operation are carried out.

On the other hand, in case of where the lean operation ( $A/F > 14.7$ ) is determined, the judgment of the existence of NOx adsorbing ability of the catalyst 18 is carried out. And it is judged when the apparatus has the existence of the adsorbing ability, the fuel injection amount for carrying out the lean operation being followed to the indication is determined. Besides, it is judged when the apparatus has no adsorbing ability, the air-fuel ratio is shifted to the rich side with a predetermined period and then the catalyst 18 is regenerated.

Fig. 8 shows a flow chart of the air-fuel ratio control. In a step 1002, signals for indicating various operation conditions or for detecting the operation conditions are read in. According to these signals, in a step 1003, the air-fuel ratio is determined, and in a step 1004 the determined air-fuel ratio is detected. In a step 1005, the size between the determined air-fuel ratio and the stoichiometric air-fuel ratio is compared.

Herein, the stoichiometric air-fuel ratio to be the comparison subjective, to put it more precisely, is the air-fuel ratio in which the velocity of the catalytic reduction reaction of NOx in the catalyst exceeds over the NOx pick-up velocity in accordance with the adsorption. This stoichiometric air-fuel ratio is determined by evaluating the characteristics of the catalyst in advance and the air-fuel ratio of the vicinity of the stoichiometric air-fuel ratio is selected.

Herein, in case where the established air-fuel ratio is equal to or less than the stoichiometric air-fuel



ratio, it proceeds to a step 1006, and without regeneration operation of the catalyst the air-fuel ratio operation followed by the indication is carried out.

5        In case where the established air-fuel ratio is more than the stoichiometric air-fuel ratio, it proceeds to a step 1007. In the step 1007, the assumption execution of NOx adsorption amount is carried out. In successively, in a step 1008, the assumed NOx adsorption  
10       amount is judged whether it is less than a predetermined limitation amount or not.

15       The limitation adsorption amount is set to a value where NOx in the exhaust gas is enable to be fully purified by evaluating NOx pick-up characteristics in the catalyst according to the beforehand experimentation carried out considering the exhaust gas temperature and the catalyst temperature etc..

20       In case where the apparatus has NOx adsorbing ability, it proceeds to a step 1006, without the regeneration operation of the catalyst the air-fuel ratio operation followed by the indication is carried out. In case where the apparatus has no NOx adsorbing ability, it proceeds to a step 1009, and the air-fuel ratio is shifted to the rich side. In step 1010, the rich shift  
25       time is counted and in case where the lapse time  $T_r$  exceeds over a predetermined time  $(T_r)_c$ , the rich shift finishes.

      The judgment of NOx adsorbing ability will be carried out as following.

30       Fig. 9 shows a method for judging and accumulating NOx discharging amount according to the various kinds operation conditions during the lean operation time.

      In a step 1007-E01, the signals relating to the

working conditions of the catalyst such as the exhaust gas temperature and signals relating to various kinds engine operation conditions which affect to NOx concentration in the exhaust gas are read in and NOx amount  $E_n$  to be absorbed in a unit time is assumed.

In a step 1007-E02, NOx amount  $E_n$  is accumulated, and in a step 1008-E01 the size between the accumulation value  $\Sigma E_n$  and the upper limitation value  $(E_n)_c$  is compared.

In case where the accumulation value  $\Sigma E_n$  is equal to or is less than the upper limitation value  $(E_n)_c$  the accumulation is continued, but in case where the accumulation value  $\Sigma E_n$  is more than the upper limitation value  $(E_n)_c$  in a step 1008-E02 the accumulation is released and it proceeds to a step 1009.

Fig. 10 shows a method for judging NOx adsorbing ability according to the accumulation time of the lean operation time.

In a step 1007-H01, the lean operation time  $H_L$  is accumulated, and in a step 1008-H01 the size between the accumulation value  $\Sigma H_L$  and the upper limitation value  $(H_L)_c$  of the accumulation time is compared.

In case where the accumulation value  $\Sigma H_L$  is equal to or is less than the upper limitation value  $(H_L)_c$  the accumulation is continued, but in case where the accumulation value  $\Sigma H_L$  is more than the upper limitation value  $(H_L)_c$  in a step 1008-H02 the accumulation is released and it proceeds to a step 1009.

Fig. 11 shows a method for judging NOx adsorbing ability according to the oxygen sensor signal during the lean operation time.

In a step 1007-O01, the oxygen amount  $Q_o$  is

accumulated, and in a step 1008-001 the size between the accumulation value  $\Sigma Q_o$  and the upper limitation value  $(Q_o)_c$  of the oxygen amount is compared.

5 In case where the accumulation value  $\Sigma Q_o$  is equal to or is less than the upper limitation value  $(Q_o)_c$  the accumulation is continued, but in case where the accumulation value  $\Sigma Q_o$  is more than the upper limitation value  $(Q_o)_c$  in a step 1008-002 the accumulation is released and it proceeds to a step 1009.

10 Fig. 12 shows a method for judging NOx adsorbing ability according to NOx concentration sensor signal which is detected in the inlet port of the catalyst during the lean operation time.

15 In a step 1007-N01, NOx amount  $Q_n$  in the inlet port of the catalyst is accumulated according to NOx concentration sensor signal. In a step 1008-N01 the size between the accumulation value  $\Sigma Q_n$  and the upper limitation value  $(Q_n)_c$  of the accumulation NOx amount is compared.

20 In case where the accumulation value  $\Sigma Q_n$  is equal to or is less than the upper limitation value  $(Q_n)_c$  the accumulation is continued, but in case where the accumulation value  $\Sigma Q_n$  is more than the upper limitation value  $(Q_n)_c$  in a step 1008-002 the accumulation is released and it proceeds to a step 1009.

25 Fig. 13 shows a method for judging NOx adsorbing ability according to NOx concentration sensor signal which is detected in the outlet port of the catalyst during the lean operation time.

30 In a step 1007-C01, NOx amount  $C_n$  in the outlet port of the catalyst is accumulated according to NOx concentration sensor signal. In a step 1008-C01 the

size between the accumulation value  $\Sigma C_N$  and the upper limitation value  $(C_N)_c$  of the accumulation NOx amount is compared.

5 In case where the accumulation value  $\Sigma C_N$  is equal to or is less than the upper limitation value  $(C_N)_c$ , the accumulation is continued, but in case where the accumulation value  $\Sigma C_N$  is more than the upper limitation value  $(C_N)_c$ , it proceeds to a step 1009.

10 Fig. 14 shows another embodiment of an exhaust gas purification apparatus according to the present invention.

The structural difference between the embodiment shown in Fig. 1 and this embodiment is a provision of manifold catalyst 17 which is arranged on the exhaust  
15 air duct at a vicinity of the engine 99.

The reinforcement for the discharging regulation of the exhaust gas in the automobile is necessary to purify the harmful materials such as HC which is discharged immediately after the engine starting time. Namely, in  
20 the prior technique the harmful materials are discharged with non-treatment until the catalyst reaches to the working temperature, but it is necessary to reduce remarkably the non-treated amount of the harmful materials.

25 To reduce widely the non-treated amount of the harmful materials, a method for abruptly arising the catalyst to the working temperature is effective.

Fig. 14 shows the apparatus construction which is enable to diminish HC and CO discharging amount during  
30 the engine starting time and also the exhaust gas purification in the lean operation time and the stoichiometric operation time (including the rich

operation time).

5 In the construction shown in Fig. 14, as the manifold catalyst 17, it can apply the three component catalyst comprised mainly of Pt, Rh, and CeO<sub>2</sub>, the material in which Pd is added to the three component catalyst, and the combustion catalyst which is comprised of the combustion active components such as Pd as a main component.

10 In this construction shown in Fig. 14, during the engine starting time the temperature of the manifold catalyst 17 arises in a short time and the purification of HC and CO is carried out immediately after the engine starting.

15 During the stoichiometric operation time both the manifold catalyst 17 and the catalyst 18 fulfill the function and then the purification for HC, CO and NO<sub>x</sub> is carried out and during the lean operation time the catalyst 18 adsorption-purifies NO<sub>x</sub>.

20 In case of the regeneration of the catalyst 18, the air-fuel ratio is shifted to the rich side, HC and CO as the gaseous reducing agent do not receive the large chemical change by the manifold catalyst 17 and can reach to the catalyst 18 and regenerates the catalyst 18. The above stated construction can obtain by the  
25 provision of the catalyst 18 and this is a remarkable feature obtained by the provision of the catalyst 18.

30 Fig. 15 shows a further embodiment of an exhaust gas purification apparatus according to the present invention. The difference between the construction shown in Fig. 1 and the construction shown in Fig. 15 resides in that the engine 99 is a direct fuel injection system. The apparatus according to the present invention, it can suitably apply to the direct fuel

injection system engine.

Fig. 16 shows a further embodiment of an exhaust gas purification apparatus according to the present invention. The difference between the constructions shown in Fig. 1 and Fig. 15 and the construction shown in Fig. 16 resides in that a post-catalyst 24 is provided at the downstream of the catalyst 18.

For example, by arranging the combustion catalyst on the post-catalyst 24 it can realize the apparatus in which HC purification ability can be improved. Further, by arranging the tree way catalyst on the post-catalyst 24 it can realize the apparatus in which the tree way function during the stoichiometric operation time can be reinforced.

Fig. 17 shows a further embodiment of an exhaust gas purification apparatus according to the present invention. The difference between the constructions shown in Fig. 1 and Figs. 14-16 and the construction shown in Fig. 17 resides in that by the indication of the rich-shift the fuel is added to the upstream of the catalyst 18 through a gaseous reducing agent injector 23. In this system, the operation conditions of the engine can be established in regardless of the conditions of the catalyst 18.

Hereinafter, the effects obtained by the present invention will be explained by illustrating embodied examples.

The inventor's of the present invention were evaluated with respect to the exhaust gas purification performances of the catalyst and of the exhaust gas purification apparatus according to the present invention.

The catalyst and the comparison catalyst were mounted

on the lean burn specification automobile having the displacement volume of 1.8 liters and the automobile was run on a chassis dynamometer.

5 Both the test catalysts were the honeycomb shape ones having 400 cell/in<sup>2</sup> and the volume of 1.7 liters and were heat-treated at 700 °C under the oxidization atmosphere and they were putted below the floor.

10 The running was constant speed running and 10-15 modes running based on Japanese exhaust gas regulation measurement method. The analysis of the exhaust gas was applied two methods, one of which was a method for measuring NO<sub>x</sub>, HC, and CO concentrations in the exhaust gas with the direct analysis using the automobile exhaust gas measurement apparatus, and another of which  
15 was a method for measuring CVS (constant volume sampling) value using the automobile constant volume dilution sampling apparatus.

Further, in 10-15 mode running, the running was the lean (A/F = 22-23) running during the constant speed  
20 running time, was the acceleration time from 20 km/h to 40 km/h at 10 mode and the acceleration time from 50 km/h to 70 km/h at 15 mode, and the rest of the running was the stoichiometric running.

Fig. 18 shows NO<sub>x</sub> concentration of the inlet port and  
25 the outlet port of the catalyst at the last 10 mode among of 10 modes being repeated three times and 15 mode succeeded to the last 10 mode in case of the mounting of the catalyst N-N9 according to the present invention, in case of the mounting of the catalyst N-K9 according to  
30 the present invention, and case of the mounting of the catalyst N-R2 according to the comparison example. The comparison catalyst had the composition shown in a latter Table 2.

In Fig. 18, in case the mounting of the catalysts N-N9 and N-K9, the outlet port NOx concentration lowered the inlet port NOx concentration at all operation areas, and since the lean operation and the stoichiometric operation were carried out repeatedly, the catalyst was regenerated effectively and NOx purification ability was held and continued. On the other hand, in the comparison catalyst N-R2, there is a portion where the outlet port NOx concentration exceeded over the inlet port NOx concentration.

CVS value obtained by the various kinds of the catalyst and the comparison catalyst in company with the catalyst compositions are shown in Table 2 and Table 3. The preparations for the catalyst and the comparison catalyst were performed by the above stated methods. However, as the preparation raw materials, barium nitrate was used as barium (Ba) and silica-sol was used as silicon (Si). It is assumed that Si exists silica (SiO<sub>2</sub>) or the complex oxide thereof.

Table 2

	marks	composition	CVS value (g/km)		
			NOx	HC	CO
compari- son  catalyst	N-R1	(0.2Rh, 2.7Pt) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.15	0.02	0.07
	N-R2	2Mg - (0.2Rh, 2.7Pt) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.15	0.02	0.04
adsorpt- ion  catalyst	N-S1	2Mg - (0.2Rh, 2.7Pt) - 30Sr - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.08	0.10	0.08
	N-S2	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 2Mg) -	0.09	0.05	0.08



	27Ce/Al <sub>2</sub> O <sub>3</sub>			
N-S3	(0.2Rh, 2.7Pt) - (30Sr, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.11	0.08	0.11
N-S4	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.10	0.07	0.09
N-S5	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.10	0.08	0.09
N-N1	2Mg - (0.2Rh, 2.7Pt) - 18Na - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.03
N-N2	2Mg - (0.2Rh, 2.7Pt) - (18Na, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.12	0.04
N-N3	(0.2Rh, 2.7Pt) - (18Na, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.07	0.16	0.10
N-N4	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.15	0.08
N-N5	(0.2Rh, 2.7Pt) - (18Na, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.10	0.12
N-N6	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.06
N-N7	2Mg - (0.2Rh, 2.7Pt) - (10Na, 10Sr) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.10	0.05
N-N8	(0.2Rh, 2.7Pt) - -(18Na, 4Ti, 2Mg) -	0.07	0.12	0.07

		27Ce/Al <sub>2</sub> O <sub>3</sub>			
N-N9	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>		0.04	0.11	0.04
N-N10	2Mg - (0.2Rh, 2.7Pt) - (10Na, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>		0.04	0.06	0.04

Table 3

	marks	composition	CVS value (g/km)		
			NOx	HC	CO
adsorption  catalyst	N-K1	2Mg - (0.2Rh, 2.7Pt) -18K - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.0 8	0.0 3
	N-K2	2Mg - (0.2Rh, 2.7Pt) -(18K, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.1 0	0.0 5
	N-K3	(0.2Rh, 2.7Pt) -(18K, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.08	0.1 1	0.0 6
	N-K4	2Mg - (0.2Rh, 2.7Pt) -(18K, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.0 8	0.0 5
	N-K5	2Mg - (0.2Rh, 2.7Pt) -(18K, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.0 8	0.0 5
	N-K6	(0.2Rh, 2.7Pt) -(18K, 10Sr) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.07	0.1 2	0.0 8
	N-K7	2Mg - (0.2Rh, 2.7Pt) -(18K, 4Ti, 2Mg) -	0.05	0.1 0	0.0 5

	27Ce/Al <sub>2</sub> O <sub>3</sub>			
N-K8	(0.2Rh, 2.7Pt) -(18K, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.1 0	0.0 7
N-K9	2Mg - (0.2Rh, 2.7Pt) -(18Na, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.0 7	0.0 4
N-K10	2Mg - (0.2Rh, 2.7Pt)- (10K, 10Sr, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.04	0.0 7	0.0 8
N-M1	2Mg - (0.2Rh, 2.7Pt) -(10Na, 10K, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.0 5	0.0 8
N-M2	2Mg - (0.2Rh, 2.7Pt) -(10Na, 10K, 10Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.0 5	0.0 8
N-M3	2Mg - (0.2Rh, 2.7Pt) -(10Na, 10K, 10Sr) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.1 0	0.0 5
N-M4	2Mg - (0.2Rh, 2.7Pt) -(10Na, 10K, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.1 1	0.0 5

As to the various kinds of the catalyst, the exhaust gas purification performances thereof were measured using the model exhaust gas.

5

#### Modified Catalysts

##### Experimentation 1:

##### (Preparation Method)

The alumina powders and alumina nitrate slurry as a precursor thereof were coated on the cordierite honeycomb (400 cell/in<sup>2</sup>), and the alumina coating

10

honeycomb was obtained, such an alumina coating  
honeycomb was coated the alumina of 150 g per the  
apparent volume of the honeycomb having 1 (one) liter.  
Cerium nitrate solution is impregnated to the obtained  
5 alumina coating honeycomb and after the honeycomb was  
dried at 200 °C, the honeycomb was calcined for 1 (one)  
hour at 600 °C.

In succession, to the honeycomb a mixture liquid  
comprised of sodium nitrate ( $\text{NaNO}_3$ ) solution and  
10 magnesium nitrate ( $\text{MgNO}_3$ ) solution was impregnated and in  
similarly the above the honeycomb was dried and calcined.

Further, the honeycomb was impregnated in a mixture  
solution comprised of dinitrodiamine platinum nitrate  
solution and rhodium nitrate ( $\text{Rh}(\text{NO}_3)_3$ ) solution, after  
15 the honeycomb was dried at 200 °C the honeycomb was  
calcined for 1 (one) hour at 450 °C. In finally,  
magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) solution was impregnated,  
after the honeycomb was dried at 200 °C the honeycomb was  
calcined for 1 (one) hour at 450 °C.

20 With the above stated method, Embodiment Catalyst 1  
was obtained, in this catalyst to 100 wt% Al, 18 wt% Ce,  
12 wt% Na, and 1.2 wt% Mg were held at the same time and  
further this Embodiment Catalyst 1 contained 1.6 wt% Pt,  
0.15 wt% Rh, and 1.5 wt% Mg.

25 Using the similar method, Embodiment Catalysts 2-4  
were obtained.

As clearly shown in above, NOx adsorption catalyst is  
provided in the exhaust gas flow passage and under the  
oxidization atmosphere of the lean gas exhaust gas NOx  
30 is caught according to the chemical adsorption and  
thereby the reduction atmosphere is formed and the  
adsorption catalyst is regenerated. Accordingly, NOx

etc. in the lean burn exhaust gas can be purified with the high efficiency without the big affect on the fuel consumption.

The compositions of the prepared catalysts are shown in Table 4 in a lamp. The support order in this Table 4 indicates that after a first component has been held, a second component and then the third and the fourth were held. Further, the supported amount is indicated at before of the support metal symbol.

Table 4

	support order			
	first component	second component	third component	fourth component
Embodi- ment Catalyst 1	18 wt% Ce	12 wt% Na 1.2 wt% Mg	0.15 wt% Rh 1.6 wt% Pt	1.5 wt% Mg
Embodi- ment Catalyst 2	18 wt% Ce	12 wt% Na 1.2 wt% Mg 7 wt% Sr	0.15 wt% Rh 1.6 wt% Pt	
Embodi- ment Catalyst 3	18 wt% La	12 wt% Na 1.2 wt% Mg	0.15 wt% Rh 1.6 wt% Pt	
Embodi- ment Catalyst 4	18 wt% Ce	1.5 wt% Na 1.5 wt% Mg	1.5 wt% Pd 1.5 wt% Pt	

(Experimentation Manner)

(1) The honeycomb shape catalyst of 6 cc (17 mm square; 21 mm length) was filled up in a Pyrex made reaction tube.

(2) The reaction tube was putted into a ring shapes electric furnace and raised to the temperature of 300 °C. As the reaction temperature, the honeycomb inlet port gas temperature was measured. After the temperature reaches to 300 °C and at the time when the temperature was stable, the flow of the model exhaust gas of the stoichiometric combustion (it is called as a stoichiometric model exhaust gas) was started. After the flow of 3 (three) minutes, the flow of the stoichiometric model gas can stopped and the flow of the model exhaust gas of the lean burn (it is called as a lean model exhaust gas) started.

NOx in the gas discharging from the reaction tube was measured according to the chemical luminescence detection method and HC was measured according to FID method.

NOx purification performance and HC purification performance obtained by this method were made as an initial period performance.

(3) The reaction tube where the honeycomb catalyst used in the above (2) was filled up was putted into the ring shape electric furnace and raised to the temperature of 300 °C. As the reaction temperature, the honeycomb inlet port gas temperature was measured.

After the temperature reached to 300 °C and became stable, the flow of the model exhaust gas of the stoichiometric combustion which contain SO<sub>2</sub> gas is as a catalyst poisoning was started. The SO<sub>2</sub> poisoning operation was finished by flowing the poisoning gas SO<sub>2</sub>.

gas 5 for (five) hours.

After the above stated  $\text{SO}_2$  poisoning sing the honeycomb catalyst, the test similar to the above (2) was carried out and  $\text{NO}_x$  purification performance and HC purification performance of after  $\text{SO}_2$  poisoning were obtained.

(4) The honeycomb catalyst used in the above (2) was putted into the baking furnace and under the air atmosphere the honeycomb catalyst was calcined at  $300^\circ\text{C}$  for 5 (five) hours. After the cooling of the honeycomb catalyst,  $\text{NO}_x$  purification performance and HC purification performance similar to the above (2) were measured.

As the stoichiometric model exhaust gas, the gas comprised of 0.1vol%  $\text{NO}$ , 0.05vol%  $\text{C}_3\text{H}_8$ , 0.6vol%  $\text{CO}$ , 0.6vol%  $\text{O}_2$ , 0.2vol%  $\text{H}_2$ , 10vol% water vapor and the balance of  $\text{N}_2$  were used.

Further, as the lean model exhaust gas, the gas comprised of 0.06vol%  $\text{NO}$ , 0.04vol%  $\text{C}_3\text{H}_8$ , 0.1vol%  $\text{CO}$ , 10vol%  $\text{CO}_2$ , 5vol%  $\text{O}_2$ , 10vol% water vapor and the balance of  $\text{N}_2$  were used.

In the above stoichiometric model exhaust gas,  $\text{C}_3\text{H}_8$ ,  $\text{CO}$ ,  $\text{H}_2$  are the gaseous reducing agents and  $\text{O}_2$  and  $\text{NO}$  are the gaseous oxidizing agents. The gaseous oxidizing agent amount is 0.65 % for converting into  $\text{O}_2$  and the gaseous reducing agent amount is 0.575 % for converting into  $\text{O}_2$  consumption ability. Accordingly, both were balanced.

In the lean mode exhaust gas,  $\text{C}_3\text{H}_8$  and  $\text{CO}$  are the gaseous reducing agents and  $\text{O}_2$  and  $\text{NO}$  are the gaseous oxidizing agents. The gaseous oxidizing agent amount is 5.03 % for converting into  $\text{O}_2$  and the gaseous reducing agent amount is of 0.23 % for converting into  $\text{O}_2$ .

consumption ability. Accordingly, there is an excess amount of oxygen ( $O_2$ ) of 4.8 %.

As the gas served to the catalyst poisoning, the gas comprised of 0.1vol%  $NO$ , 0.05vol%  $C_3H_6$ , 0.6vol%  $CO$ , 0.005vol%  $SO_2$ , 10vol% water vapor and the balance of  $N_2$  were used.

The space velocities of the above three kinds gases were 30,000 /h in the dry gas base (not containing the water vapor).

Table 5 shows the purification rate of the honeycomb catalyst of the initial period and after the poisoning by  $SO_2$ . Here,  $NO_x$  purification rate was obtained after 1 (one) minute where the stoichiometric model gas was changed over to the lean model exhaust gas.

Table 5

	initial $NO_x$ purification rate (%)		$NO_x$ purification rate (%) after poisoning by $SO_2$		$NO_x$ purification rate (%) after 800 °C calcination	
	300 °C	400 °C	300 °C	400 °C	300 °C	400 °C
Embodiment Catalyst 1	91	94	76	67	58	49
Embodiment Catalyst 2	98	97	85	70	67	62
Embodiment Catalyst 3	91	94	75	65	55	45
Embodiment Catalyst 4	90	90	70	60	55	45



NOx purification rate and HC purification rate were calculated according to following formula.

NOx purification rate = (NOx concentration in inlet port gas - NOx concentration in outlet port gas) x 100 / (NOx concentration in inlet port gas) .....(1)

HC purification rate = (HC concentration in inlet port gas - HC concentration in outlet port gas) x 100 / (HC concentration in inlet port gas) .....(2)

Embodiment Catalysts 1-4 had a high initial period performance and a heat resistant ability and a SOx endurance ability.

Embodiment Catalyst 5 was obtained by replacing the support material of Embodiment Catalyst 1 with La and Al complex oxide material (La- $\beta$ -Al<sub>2</sub>O<sub>3</sub>) where the construction ratio La-Al comprised of 1-20 mol% La and 100 mol% sum of La and Al. The performances of Embodiment Catalyst 5 are shown in Table 6.

Table 6

	initial NOx purification rate (%)		Nox purification rate (%) after poisoning by SO <sub>2</sub>		NOx purification rate (%) after calcination at 800 °C	
	300 °C	400 °C	300 °C	400 °C	300 °C	400 °C
Embodiment Catalyst 5	90	88	75	65	67	65

As the support was constituted by La-Al complex oxide material ( $\text{La-}\beta\text{-Al}_2\text{O}_3$ ), the heat resistant ability can be improved.

5 In Embodiment Catalyst 1, the initial period performance of NOx purification rate at 400 °C, in which the support amount of Na of the second component was varied, was measured. The catalyst preparation manner was similar to Embodiment Catalyst 1 and the experimentation manner was similar to the  
10 Experimentation 1. The results are shown in Fig. 21. To obtain the high NOx purification rate, it was suitable to make Na supported amount which was 5-20 wt% to the support of 100 wt%.

In Embodiment Catalyst 1, the initial period  
15 performance of NOx purification rate at 400 °C, in which the supported amount at Mg of the second component was varied was measured. The results are shown in Fig. 22. To obtain the high NOx purification rate, it was suitable to make the weight ratio between Mg supported  
20 amount and (Na supported amount + Mg support amount) at 1-40 wt%.

In Embodiment Catalyst 1, the initial period performance of NOx purification rate at 400 °C, in which the supported amount of Ce of the first component was  
25 varied, was measured. The results are shown in Fig. 23. To obtain the high NOx purification rate, it was suitable to make Ce supported amount at 5-30 wt%.

In Embodiment Catalyst 1, the initial period performance of NOx purification rate at 400 °C, in which  
30 the supported amounts of Pt and Rh were varied, was measured. The results are shown in Fig. 24. To obtain the high NOx purification rate, it was suitable to make

the supported amount of Pt at 0.5-3 wt% and the supported amount of Rh at 0.05-0.3 wt%.

In Embodiment Catalyst 1, the initial period performance of NOx purification rate at 400 °C, in which the supported amounts of Pt and Pd were varied, was measured. The results are shown in Fig. 25. To obtain the high NOx purification rate, it was suitable to make the supported amount of Pt at 0.5-3 wt% and the supported amount of Pd at 0.5-15 wt%.

In Embodiment Catalyst 2, NOx purification rate at 400 °C of the initial period and after the calcination at 800 °C, was measured. The results are shown in Fig. 26. Since the supported amount of Sr was 1-20 wt%, the high NOx purification rate and the high heat resistant ability were obtained.

#### Experimentation 2: (Preparation Method)

Water and dilute nitric acid are added to boehmite powers and slurry for coating was obtained. The obtained slurry was wash-coated to a cordierite made honeycomb and after drying the honeycomb was calcined for 1 (one) hour at 600 °C, thereby an alumina coating honeycomb was obtained. Coated amount of alumina was 150 g per the honeycomb 1 litter.

The above alumina coated honeycomb was immersed in Ce nitrate solution and after drying the honeycomb was calcined for 1 (one) hour at 600 °C. In succession, the honeycomb was immersed in Sr nitrate solution and after drying the honeycomb was calcined for 1 (one) hour at 600 °C. Further, the honeycomb was immersed in titania-sol solution as a precursor for titania and after drying

the honeycomb was calcined for 1 (one) hour at 600 °C.

Next, the honeycomb was immersed in a solution containing dinitrodiamime Pt nitrate and Rh nitrate and after drying the honeycomb was calcined for 1 (one) hour at 450 °C. Finally, the honeycomb was immersed in Mg nitrate solution and after drying the honeycomb was calcined for 2 (two) hours at 450 °C, then honeycomb A was obtained.

The catalyst composition of the honeycomb catalyst A was comprised of to alumina ( $\text{Al}_2\text{O}_3$ ) of 100 wt%, Mg of 1 wt%, Rh of 0.15 wt%, Pt of 1.9 wt%, Ti of 5 wt%, Sr of 15 wt%, and Ce of 18 wt% and this is the standard for other Embodiment Catalysts.

Further, as the method for manufacturing the honeycomb catalyst, in addition to the above method of impregnating the catalyst components to the alumina coated honeycomb, it is possible to employ a method where the catalyst components are immersed into the aluminum powders and after the catalyst powders are prepared they are made to the slurry, the slurry are coated to the honeycomb substrate (honeycomb base body). Further, as the precursor of titania, in addition to the above titania-sol, it can employ an organo titanium compound, the titanium sulfate and the titanium chloride etc. As the alkali earth metals in place of Sr nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) using Ca nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), a honeycomb catalyst B was obtained.

Except for as the rare earth metals in place of cerium nitrate ( $\text{Ce}(\text{NO}_3)_3$ ) using lanthanum nitrate ( $\text{La}(\text{NO}_3)_3$ ), using the similar method shown in the honeycomb catalyst A, a honeycomb catalyst C was obtained. Further, using iridium nitrate, a honeycomb

catalyst D was obtained.

According to the variations of the concentration of the titania-sol used in the preparation of the honeycomb catalyst A, three kinds honeycomb catalysts E, F and G having different Ti supported amount were obtained.

According to the variations of the concentration of strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) used in the preparation of the honeycomb catalyst A, three kinds honeycomb catalysts H, I and J having different Sr supported amount were obtained.

According to the variations of the concentration of dinitrodiamine Pt solution used in the preparation of the honeycomb catalyst A, three kinds honeycomb catalysts K, L and M having different Pt supported amount were obtained.

According to the variations of the concentration of rhodium nitrate solution used in the preparation of the honeycomb catalyst A, three kinds honeycomb catalysts N, O and P having different Rh supported amount were obtained.

According to the variations of the concentration of cerium nitrate solution used in the preparation of the honeycomb catalyst A, three kinds honeycomb catalysts Q, R and S having different Ce supported amount were obtained.

A honeycomb catalyst T was obtained, this honeycomb T do not contain titanium (Ti) in the honeycomb catalyst A.

The catalyst compositions of the honeycomb catalysts A-T are shown in Table 7 in a lump.

Table 7

catalyst composition (wt%)									NOx purification rate (%)	
	rare earth		alkali earth		Ti	Pt	Rh	Mg	initial period	after SO <sub>2</sub> endurance
A	Ce	18	Sr	15	5	1.9	0.15	1	83	77
B	Ce	18	Ca	15	5	1.9	0.15	1	82	72
C	La	18	Sr	15	5	1.9	0.15	1	80	73
D	Y	18	Sr	15	5	1.9	0.15	1	81	72
E	Ce	18	Sr	15	0.1	1.9	0.15	1	80	71
F	Ce	18	Sr	15	1	1.9	0.15	1	81	73
G	Ce	18	Sr	15	30	1.9	0.15	1	80	72
H	Ce	18	Sr	3	5	1.9	0.15	1	80	70
I	Ce	18	Sr	7.5	5	1.9	0.15	1	82	75
J	Ce	18	Sr	40	5	1.9	0.15	1	81	72
K	Ce	18	Sr	15	5	0.2	0.15	1	80	69
L	Ce	18	Sr	15	5	1	0.15	1	81	73
M	Ce	18	Sr	15	5	4	0.15	1	85	76
N	Ce	18	Sr	15	5	1.9	0.15	1	80	73
O	Ce	18	Sr	15	5	1.9	0.5	1	82	74
P	Ce	18	Sr	15	5	1.9	1	1	81	72
Q	Ce	5	Sr	15	5	1.9	0.15	1	80	70
R	Ce	10	Sr	15	5	1.9	0.15	1	82	73
S	Ce	40	Sr	15	5	1.9	0.15	1	84	72
T	Ce	18	Sr	15	0	1.9	0.15	1	80	69

## Test Manner 1:

5 As to the honeycomb catalysts A-T, under following conditions, NOx purification reaction activity was evaluated.

A honeycomb catalyst having 6 cc was filled up in a

quartz reaction tube having an inner diameter of 25 mm and was arranged in an electric furnace.

The reaction tube was heated according to the electric tube and an inlet port gas temperature of the reaction tube was made to be 300 °C constant and a following model gas was let flow.

As the exhaust gas being supposed in a condition where an internal combustion engine was operated with the stoichiometric air-fuel ratio, the model gas had composition comprised of 0.1% (volume ratio) NO, 0.05% C<sub>3</sub>H<sub>8</sub>, 0.6% CO, 0.5% O<sub>2</sub>, 0.2% H<sub>2</sub>, 10% H<sub>2</sub>O, and the balance of N<sub>2</sub> and this model gas was flowed at a space velocity of 30,000 /h.

As the exhaust gas being supposed in a condition where an internal combustion engine was operated with the lean air-fuel ratio, the model gas had composition comprised of 0.06% (volume ratio) NO, 0.04% C<sub>3</sub>H<sub>8</sub>, 0.1% CO, 5% O<sub>2</sub>, 10% H<sub>2</sub>O, and the balance of N<sub>2</sub> and this model gas was flowed at a space velocity of 30,000 /h. The above model gas supposed having the stoichiometric air-fuel and the above model gas supposed having the lean air-fuel ratio were flowed alternatively every three (3) minutes each.

In these model exhaust gases, the gaseous oxidizing agent amount is 0.55 vol% for converting into O<sub>2</sub> and the gaseous reducing agent amount of 0.625 for converting into O<sub>2</sub> consumption ability. Accordingly, both were almost balanced.

The model gas supposed the stoichiometric air-fuel ratio and the model gas supposed the lean air-fuel ratio were flowed alternatively every three (3) minutes each.

The inlet port NO<sub>x</sub> concentration and the outlet port NO<sub>x</sub> concentration of the catalyst at this time were

measured according to the chemical luminescence  
detection NOx analyzer. And NOx purification rate after  
1 minute when the stoichiometric air-fuel ratio model  
exhaust gas was changed to the lean air-fuel ratio model  
5 exhaust gas was calculated according to a formula shown  
in Experimentation 1.

Test Manner 2:

Except for that the inlet port gas temperature was  
heated by the electric furnace at 400 °C constant,  
10 according to a manner similar to Test Manner 1, as to  
each of the honeycomb catalysts A-T, NOx purification  
reaction activity was evaluated.

Test Manner 3:

Similar to Test Manner 1, the inlet port gas  
15 temperature was heated by the electric furnace at 300 °C  
constant. The gas, in which to the model gas supposed  
the lean air-fuel ratio 0.005 % SO<sub>2</sub> gas was added, was  
flowed at a space velocity of 30,000 /h for 3 (three)  
hours. After that, according to a manner similar to  
20 Test Manner 1, as to the honeycomb catalysts A-T, NOx  
purification reaction activity under the inlet port gas  
temperature of 300 °C was evaluated.

Test Manner 4:

Similar to Test Manner 3, the gas, in which to the  
25 model gas supposed the lean air-fuel ratio 0.005 % SO<sub>2</sub>,  
gas was added, was flowed at 300 °C for 3 (three) hours.  
After that, according to a manner similar to Test Manner  
2, as to the honeycomb catalysts A-T, NOx purification  
reaction activity under the inlet port gas temperature  
30 of 400 °C was evaluated.

With respect to the honeycomb catalysts A-T, the  
results of the evaluations according to Test Manners 1



and 3 are shown in Table 7 and the results of the evaluations according to Test Manners 2 and 4 are shown in Table 8.

5 Table 8

catalyst composition (wt%)									NOx purification rate (%)	
	rare earth		alkali earth		Ti	Pt	Rh	Mg	initial period	after SO <sub>2</sub> endurance
A	Ce	18	Sr	15	5	1.9	0.15	1	76	55
B	Ce	18	Ca	15	5	1.9	0.15	1	73	54
C	La	18	Sr	15	5	1.9	0.15	1	74	51
D	Y	18	Sr	15	5	1.9	0.15	1	70	48
E	Ce	18	Sr	15	0.1	1.9	0.15	1	67	45
F	Ce	18	Sr	15	1	1.9	0.15	1	72	50
G	Ce	18	Sr	15	30	1.9	0.15	1	74	53
H	Ce	18	Sr	3	5	1.9	0.15	1	67	46
I	Ce	18	Sr	7.5	5	1.9	0.15	1	72	49
J	Ce	18	Sr	40	5	1.9	0.15	1	77	54
K	Ce	18	Sr	15	5	0.2	0.15	1	65	44
L	Ce	18	Sr	15	5	1	0.15	1	70	51
M	Ce	18	Sr	15	5	4	0.15	1	80	54
N	Ce	18	Sr	15	5	1.9	0.15	1	66	45
O	Ce	18	Sr	15	5	1.9	0.5	1	76	52
P	Ce	18	Sr	15	5	1.9	1	1	72	48
Q	Ce	5	Sr	15	5	1.9	0.15	1	68	44
R	Ce	10	Sr	15	5	1.9	0.15	1	72	50
S	Ce	40	Sr	15	5	1.9	0.15	1	75	52
T	Ce	18	Sr	15	0	1.9	0.15	1	65	43

Each of Embodiment catalysts A-S has a high NOx

purification rate after SO<sub>2</sub> endurance and a strong SO<sub>2</sub> resistivity in comparison with the catalyst T which does not contain titanium (Ti).

5 As to the honeycomb catalyst A, a X-ray analyzing spectrum was measured and the crystallization structure was identified. In the X-ray analyzing spectrum of the honeycomb catalyst A, there was no peak caused by titania (TiO<sub>2</sub>) and it was considered that titania (TiO<sub>2</sub>) was maintained a non-crystalline structure. It was  
10 understood that strontium (Sr) as alkali earth metals was held as carbonate.

#### Experimentation 3:

15 Cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>) solution was impregnated in alumina (Al<sub>2</sub>O<sub>3</sub>) and after drying at 200 °C the alumina was calcined at 600 °C for 1 hour. In succession, a mixture solution obtained by mixing strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>) with silica-sol was impregnated, similarly in the cerium (Ce) coated alumina was dried and calcined.  
20 With the above process, the catalyst powders were obtained, such catalyst powders were comprised of, to 100 wt% alumina (Al<sub>2</sub>O<sub>3</sub>), 18 wt% Ce, 15 wt% Sr, 4 wt% SiO<sub>2</sub>, 1.6 wt% Pt, 0.15 wt% Rh, and 1.5 wt% Mg. Alumina-sol and aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>) were added to the  
25 catalyst powders and the slurry was obtained by agitating and mixed with them and the obtained slurry was coated to a cordierite made honeycomb (400 cell/in<sup>2</sup>). The calcination temperature was about 450 °C and Embodiment Catalyst 100 having a final coating amount of  
30 200 g/l.

According to the method similarly to the above, Embodiment Catalysts 100-105 were obtained.

The composition of the prepared catalysts are shown in Table 9. In Table 9, the support order in this Table 9 indicates that after a first component has held, a second component is held and next a third component and a fourth component are held successively. Further, the supported amount is indicated at before of the supported metal symbol.

Table 9

Embodiment Catalyst	support order			
	first component	second component	third component	fourth component
100	18 wt% Ce	15 wt% Sr 4 wt% SiO <sub>2</sub>	0.15 wt% Rh 1.6 wt% Pt	1.5 wt% Mg
101	18 wt% Ce	15 wt% Sr 4 wt% SiO <sub>2</sub>	0.15 wt% Rh 1.6 wt% Pt	
102	18 wt% Ce	7 wt% Sr 7 wt% Ca 4 wt% SiO <sub>2</sub>	0.15 wt% Rh 1.6 wt% Pt	
103	18 wt% Ce	15 wt% Sr	0.15 wt% Rh 1.6 wt% Pt	
104	18 wt% Ce	15 wt% Ca	0.15 wt% Rh 1.6 wt% Pt	
105	18 wt% Ce	7 wt% Sr 7 wt% Ca	0.15 wt% Rh 1.6 wt% Pt	

The testing manner was similarly to (1), (2) and (3) shown in Experimentation 1 and further the composition of the model gas was similarly to that of shown in Experimentation 1.

Table 10 shows NOx gas purification rate of after 1 (one) minute from the start of flow the stoichiometric model exhaust gas and the purification rate of after one minute from the start of the lean model exhaust gas obtained by the honeycomb catalyst which are initial period and after SO<sub>2</sub> poisoning. NOx gas purification rate was calculated following to the formula shown in Experimentation 1.

10 Table 10

Embodiment Catalyst	initial period NOx purification rate (%)		NOx purification rate (%) poisoning by SO <sub>2</sub>		
	stoichio -metric	lean	stoichio -metric	lean	lowering rate (%) of lean to initial
100	100	80	100	75	- 6
101	100	50	100	43	-14
102	100	65	100	59	- 9
103	100	65	100	50	-23
104	100	47	100	32	-32
105	100	58	100	40	-31

Further, the lowering rate of the lean NOx gas purification rate by SO<sub>2</sub> poisoning was calculated by the following formula.

15 Lowering rate of NOx gas purification rate =  
 (initial period NOx gas purification rate -  
 NOx gas purification rate after SO<sub>2</sub>  
 poisoning) / (initial period NOx gas

purification rate ..... formula (2)

The lowering rate of the lean NOx gas purification rate by SO<sub>2</sub> poisoning according to the support of SiO<sub>2</sub> is improved at -5% - -15%.

- 5 In Embodiment Catalyst 100, in case where SiO<sub>2</sub> supported amount was varied NOx gas purification rate was measured. The catalyst preparation manner and the experimental manner were similarly to those of Embodiment Catalyst 100. The results are shown in Table
- 10 11. By supporting SiO<sub>2</sub>, the initial period NOx gas purification rate is improved. Further, the support amount of SiO<sub>2</sub> was 0.6 wt% - 5 wt%, NOx gas purification rate after SO<sub>2</sub> poisoning can obtain 60 %.

15 Table 11

SiO <sub>2</sub> supported amount (wt%)	initial period NOx purification rate (%)		NOx purification rate (%) after SO <sub>2</sub> poisoning	
	stoichiometric	lean	stoichiometric	lean
0	100	55	100	50
0.5	100	55	100	50
0.8	100	70	100	63
1	100	75	100	68
2	100	80	100	75
3	100	80	100	75
4	100	78	100	72
5	100	65	100	60
8	100	50	100	53
9	100	55	100	49
10	100	50	100	46

## CLAIMS

1. An exhaust gas purification apparatus for use in an internal combustion engine comprising:

- 5       an exhaust gas duct connected to the engine through which the exhaust gas containing NOx gas passes and  
      a catalyst so disposed in said exhaust gas duct that it contacts with the exhaust gas, wherein  
      said catalyst chemically adsorbs NOx under the  
10       condition that a stoichiometric amount of a gaseous oxidizing agent present in the exhaust gas is larger than that of a gaseous reducing agent present in the exhaust gas for reducing NOx, while NOx being adsorbed is catalytically reduced in the presence of said  
15       reducing agent under the condition that the stoichiometric amount of said oxidizing agent is not larger than that of said reducing agent.

2. An apparatus for purifying an exhaust gas from an internal combustion engine comprising:

- 20       an exhaust gas duct connected to the engine through which the exhaust gas containing NOx gas passes, and  
      a catalyst so disposed in said exhaust gas duct that it contacts with the exhaust gas, wherein  
25       said catalyst adsorbs NOx under the condition that an amount of a gaseous oxidizing agent present in the exhaust gas is larger than that of a gaseous reducing agent added to the exhaust gas for NOx in a stoichiometric relation, while NOx being adsorbed is  
30       catalytically reduced in the presence of said reducing agent under the condition that the amount of said oxidizing agent is not larger than that of said reducing agent in the stoichiometric relation.

3. An apparatus for purifying an exhaust gas from an internal combustion engine comprising:

an exhaust gas duct connected to the engine through  
5 which the exhaust gas containing NOx gas passes, and  
a catalyst so disposed in said exhaust gas duct that  
it contacts with the exhaust gas, wherein

said catalyst adsorbs NOx under the condition that a  
stoichiometric amount of a gaseous oxidizing agent  
10 present in a lean combustion exhaust gas is larger than  
that of a gaseous reducing agent present in the lean  
combustion exhaust gas for reducing NOx, while NOx being  
adsorbed is catalytically reduced in the presence of  
said reducing agent under the condition that a  
15 stoichiometric amount of said oxidizing agent is not  
larger than that of said reducing agent in a stoichiometric  
or fuel rich combustion exhaust gas.

4. An apparatus for purifying an exhaust gas from an  
20 internal combustion engine comprising:

an exhaust gas duct connected to the engine through  
which the exhaust gas containing NOx gas passes,  
a device for controlling an air-fuel ratio of the  
exhaust gas, and

25 a catalyst so disposed in said exhaust gas duct that  
it contacts with the exhaust gas, wherein

the air-fuel ratio is switched from the condition  
that said catalyst chemically adsorbs NOx under in the  
lean combustion exhaust gas to the condition that to the  
30 condition that NOx being adsorbed is catalytically  
reduced in the presence of said reducing agent in a  
stoichiometric or fuel rich combustion exhaust gas.

5. An exhaust gas purification apparatus according to claim 1, 2, 3 or 4, wherein

the apparatus further comprises a timing establishment unit which outputs a timing signal to determine a period during which the stoichiometric amount of said reducing agent in the exhaust gas is larger than that of said oxidizing agent.

6. An exhaust gas purification apparatus according to claim 1, 2, 3 or 4, wherein

said catalyst comprises at least one of alkali metals, at least one of alkali earth metals other than barium and at least one of noble metals.

7. An exhaust gas purification apparatus according to claim 6, wherein

said catalyst further comprises at least one of titanium and silicon.

8. An exhaust gas purification apparatus according to claim 6, wherein

said catalyst further comprises at least one of rare earth metals.

9. An exhaust gas purification apparatus according to claim 1, 2, 3 or 4, wherein

said catalyst comprises a heat resistant carrier body and catalytic compounds supported on said carrier body and comprising at least one of sodium and potassium, at least one of magnesium, strontium and calcium, and at least one of platinum, palladium and rhodium.

10. An exhaust gas purification apparatus according to



claim 1, 2, 3 or 4, wherein

5       said catalyst comprises a base member, a heat  
resistant carrier body supported on said base member and  
catalytic compounds supported on said carrier body and  
comprising at least one of sodium and potassium, at  
least one of magnesium, strontium and calcium, and at  
least one of platinum, palladium and rhodium.

10       11. An exhaust gas purification apparatus according to  
claim 1, 2, 3 or 4, wherein

15       said reducing agent to be added to the lean  
combustion exhaust gas is at least one of gasoline,  
light oil, kerosene, natural gas, their reformed  
substances, hydrogen, alcohol, ammonia gas, engine blow-  
by gas and canister purging gas.

12. An exhaust gas purification apparatus according to  
claim 11, wherein

20       said reducing agent is supplied to the lean  
combustion exhaust gas in response to signals from said  
stoichiometric establishing unit.

13. An exhaust gas purification apparatus according to  
claim 1, 2, 3 or 4, wherein

25       the apparatus further comprises a manifold catalyst  
disposed in said exhaust gas duct immediately after the  
engine at the upstream of said catalyst, said catalyst  
having functions of a three component catalyst and a  
combustion catalyst.

30       14. An exhaust gas purification apparatus according to  
claim 13, wherein

      said second catalyst is disposed in said exhaust gas

duct of a fuel direct injection in-cylinder engine.

15. An exhaust gas purification apparatus according to claim 1, 2, 3 or 4, wherein

5       the apparatus further comprises a three component catalyst or a combustion catalyst is disposed in said exhaust gas duct at the upstream of said catalyst.

10 16. An apparatus for purifying an exhaust gas from an internal combustion engine comprising:

      an exhaust gas duct connected to the engine through which the exhaust gas containing NO<sub>x</sub>, SO<sub>x</sub> and oxygen passes, and

15       a catalyst which chemically adsorbs NO<sub>x</sub> under the condition that the exhaust gas is emitted from lean combustion, and NO<sub>x</sub> being adsorbed is catalytically reduced under the condition that a gaseous reducing agent is added to the lean combustion exhaust gas in such an amount that a stoichiometric amount that a  
20       stoichiometric amount of oxygen is not larger than that of said reducing agent, wherein

      said catalyst adsorbs or absorbs in the lean condition and releases SO<sub>x</sub> in the stoichiometric or rich condition.

25

17. A catalyst for purifying an exhaust gas from an internal combustion engine which comprises:

      a base member,

30       a heat resistant carrier body supported on said base member, and

      catalyst components supported on said carrier body, said carrier body having a number of small hollows extending in the direction of gas flow of the exhaust

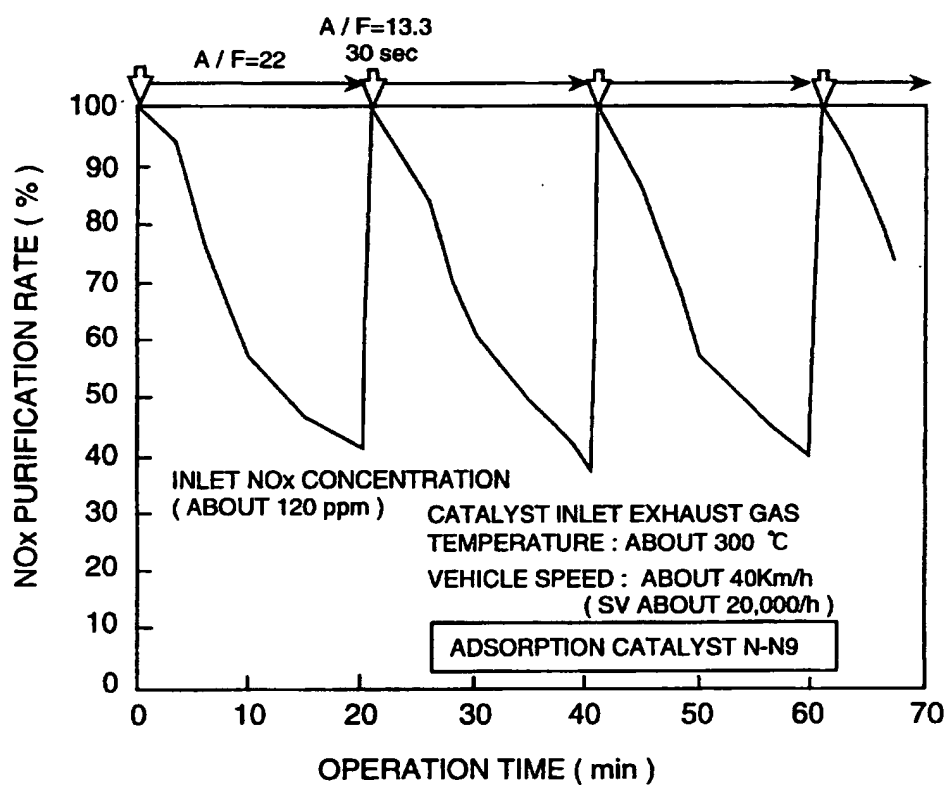
gas, wherein

said catalyst compounds comprises at least one of  
alkali metals, at least one of alkali earth metals other  
than barium, at least one of noble metals and at least  
one of rare earth metals.

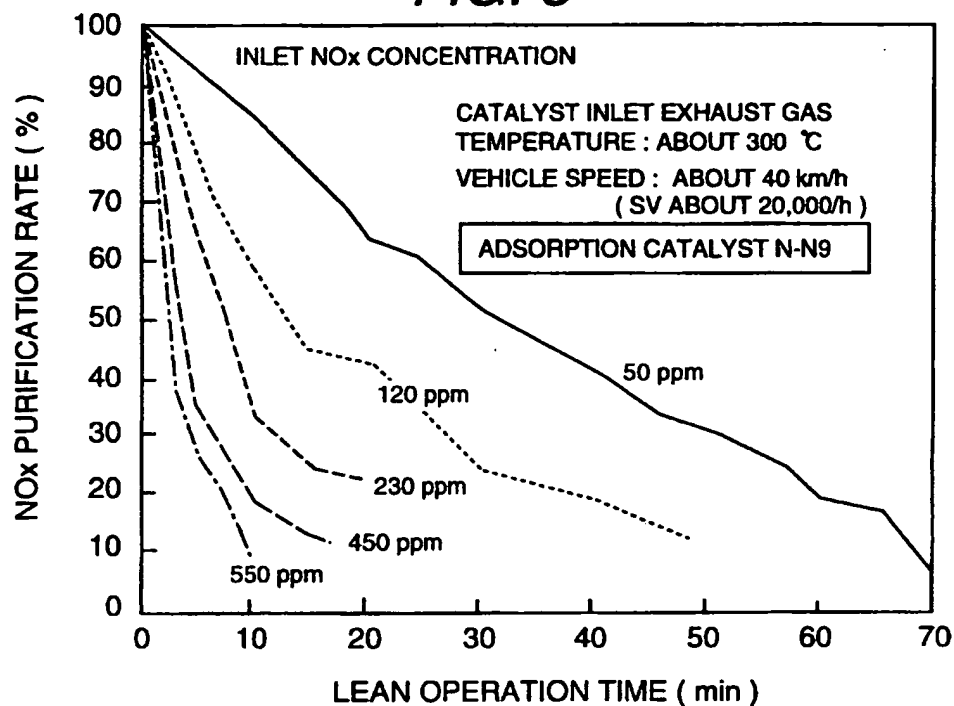
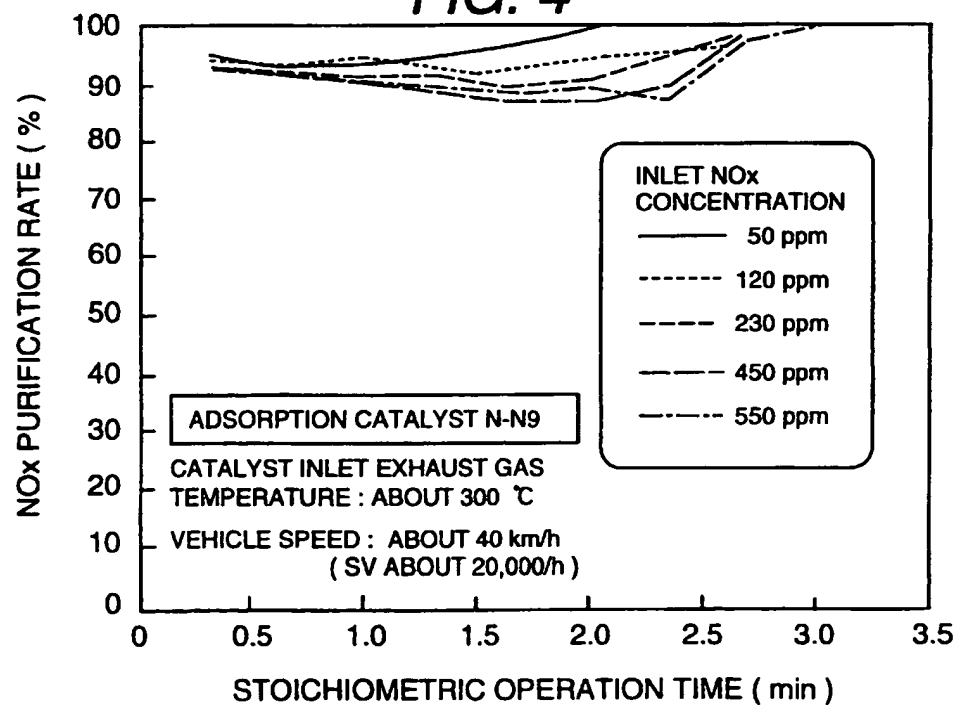
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FIG. 2



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**FIG. 3****FIG. 4**

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FIG. 5A

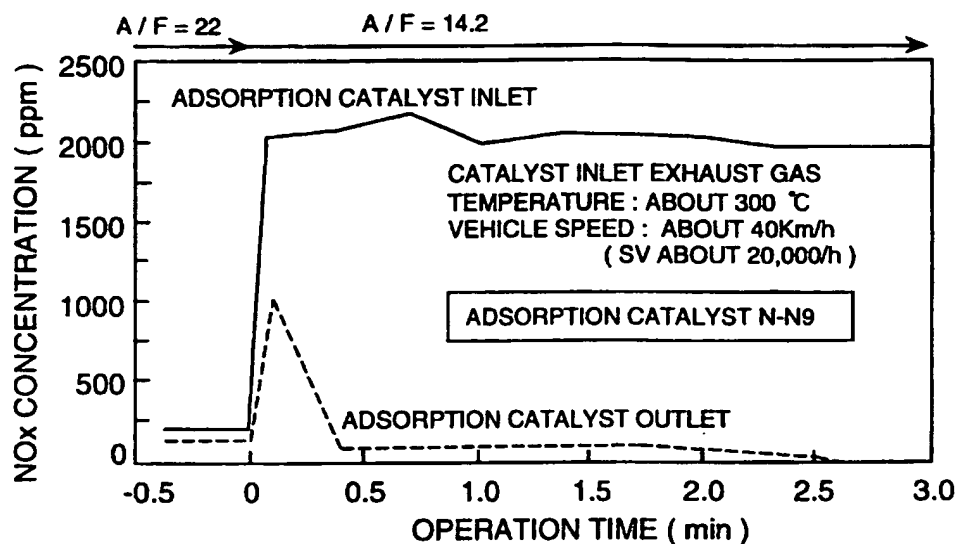
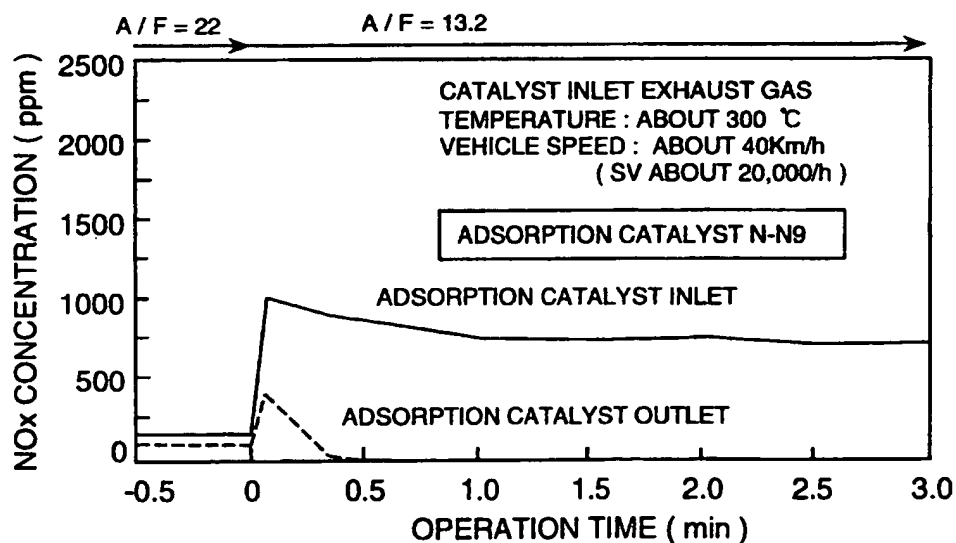


FIG. 5B



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FIG. 6A

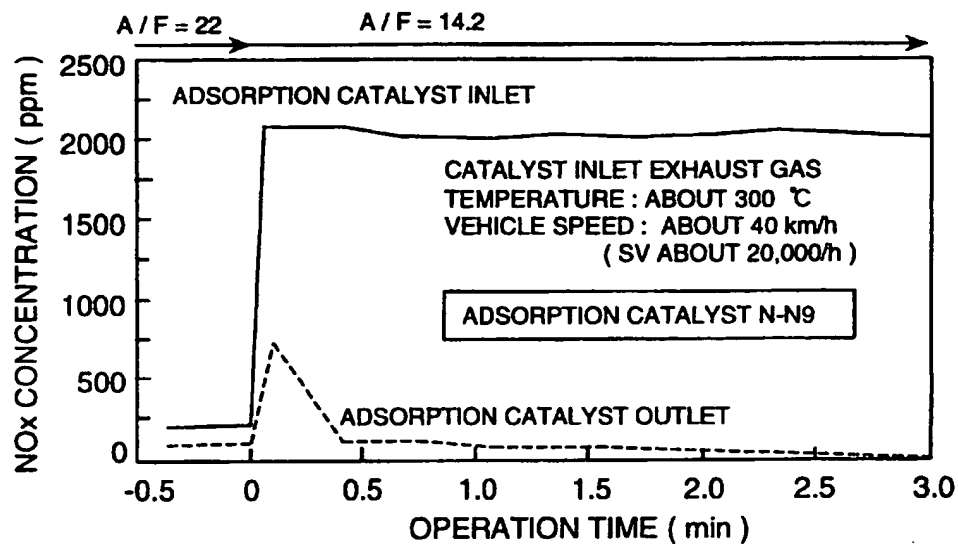
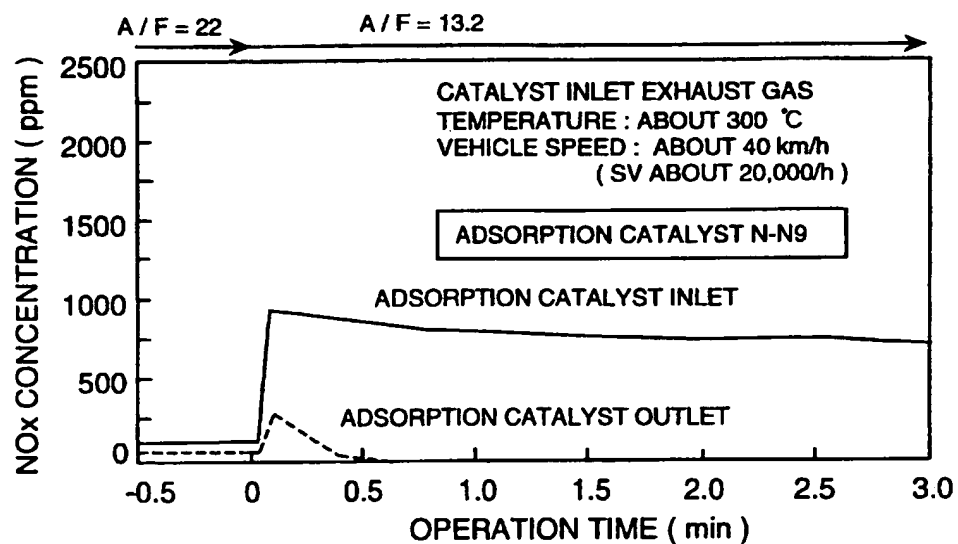


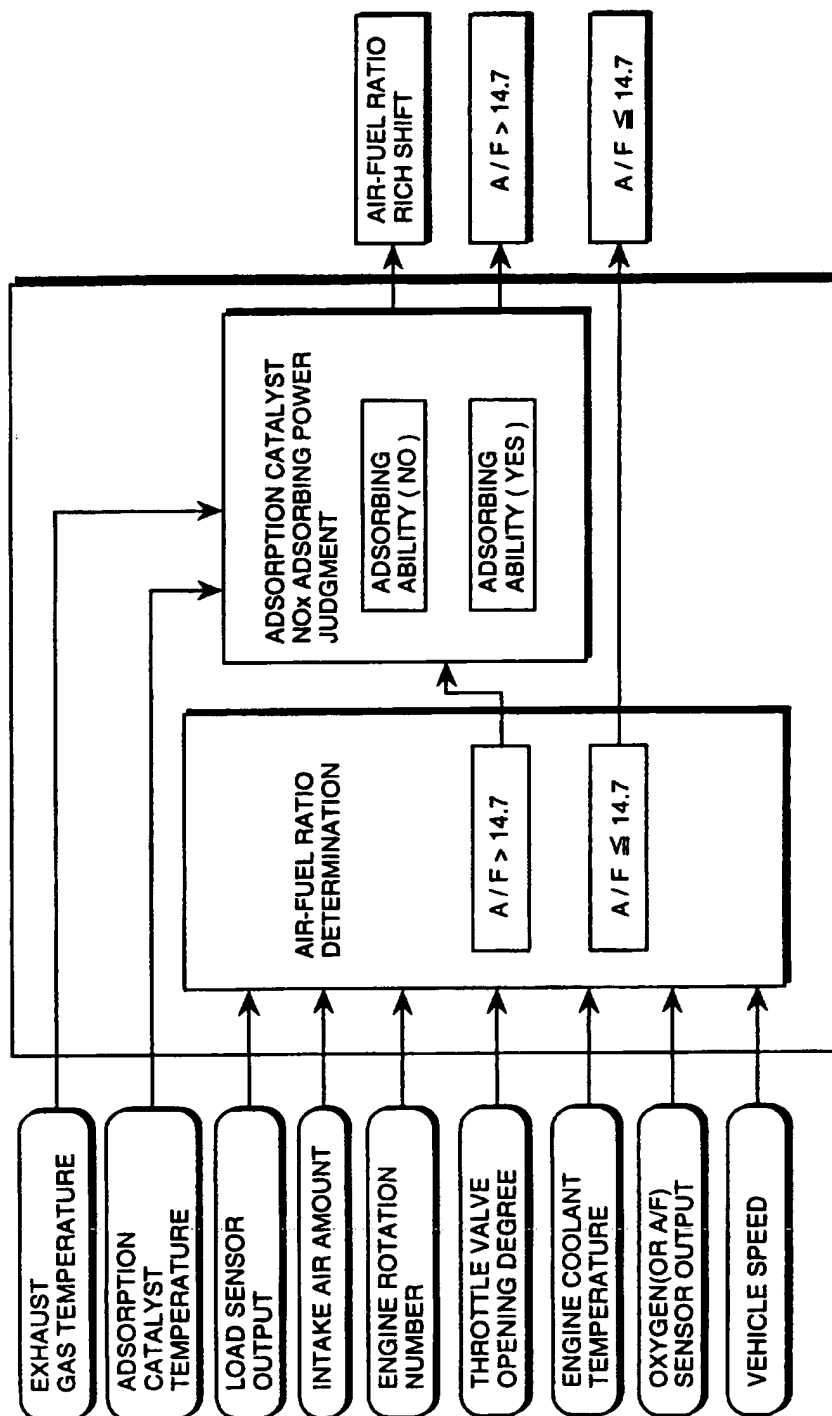
FIG. 6B





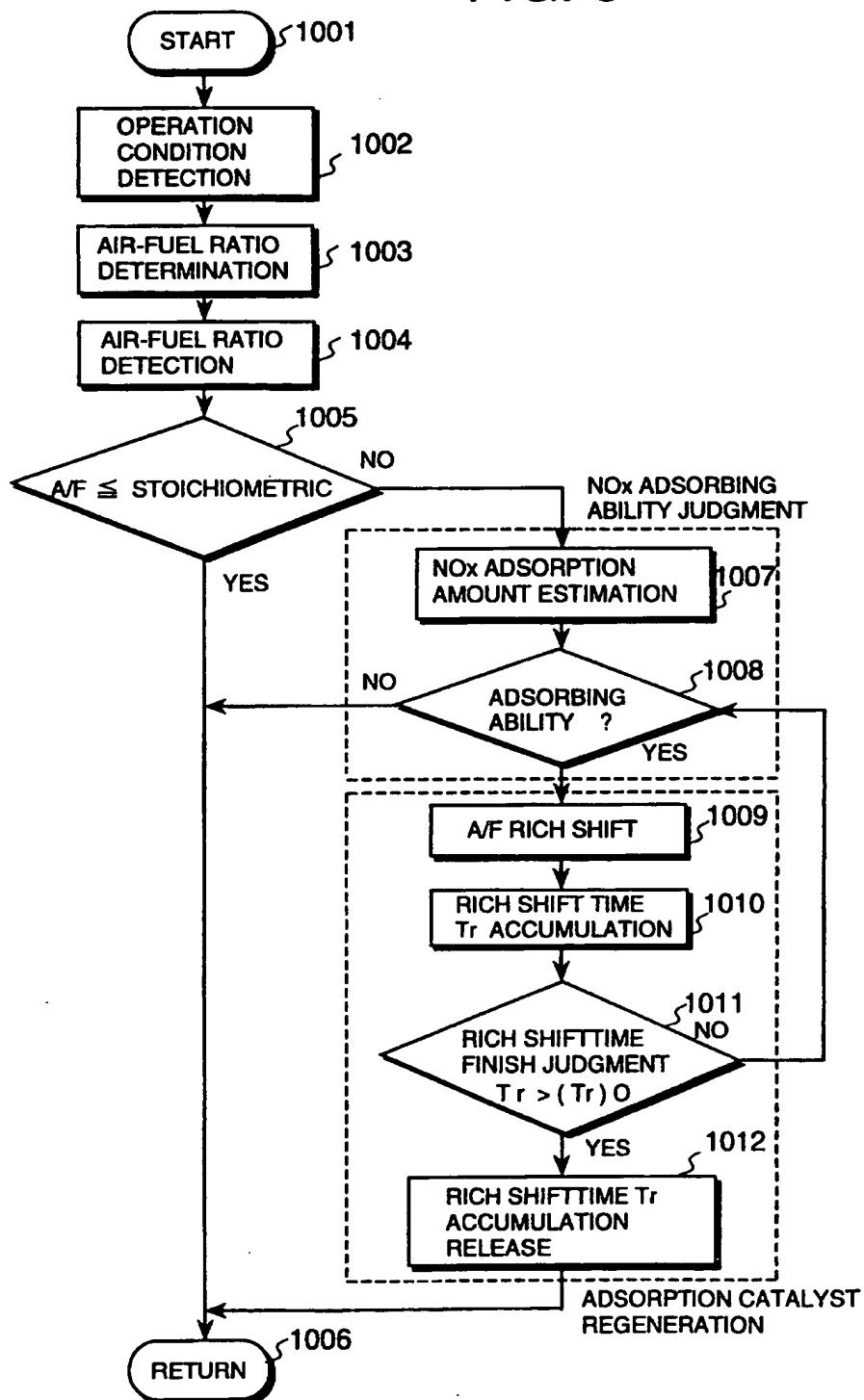
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FIG. 7



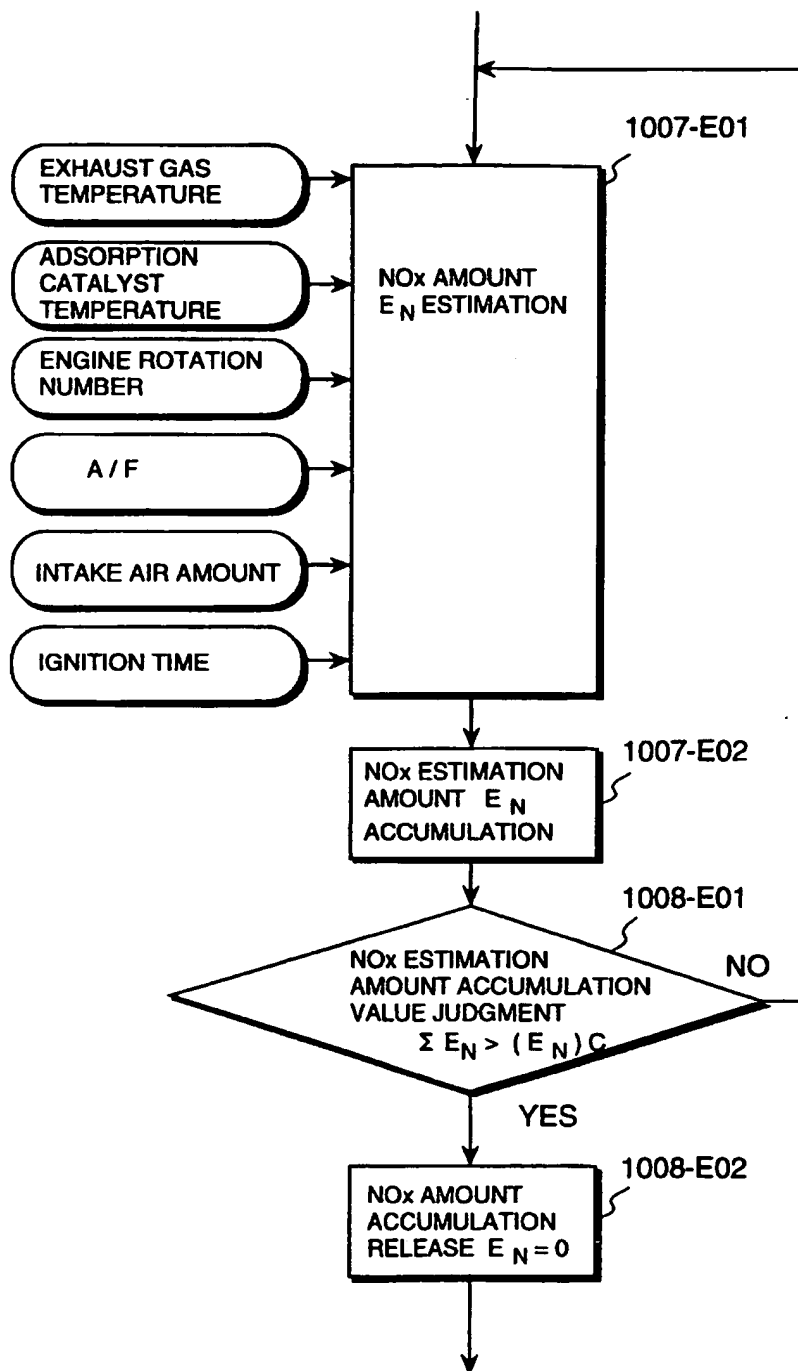
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FIG. 8



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FIG. 9



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FIG. 10

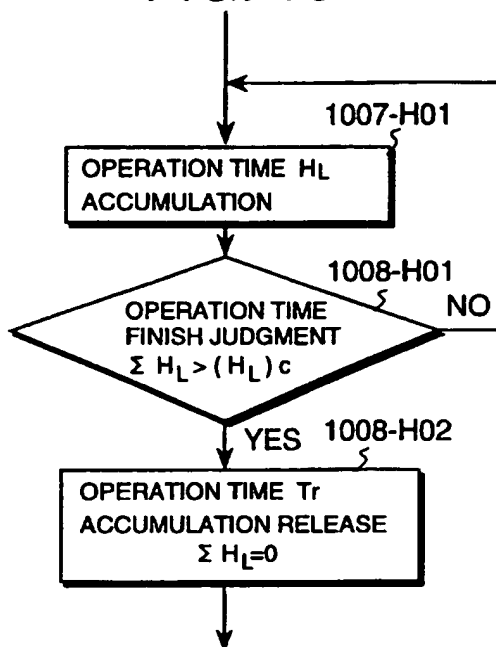
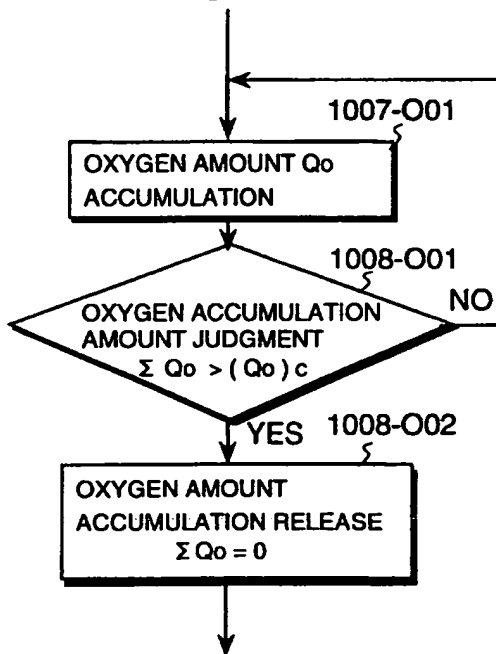


FIG. 11



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FIG. 12

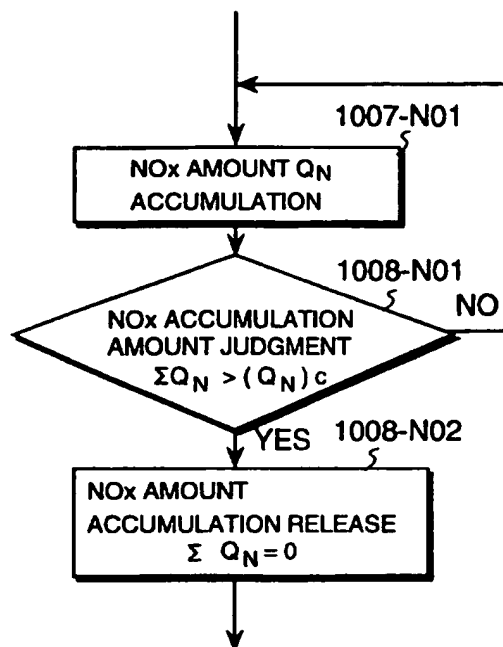


FIG. 13

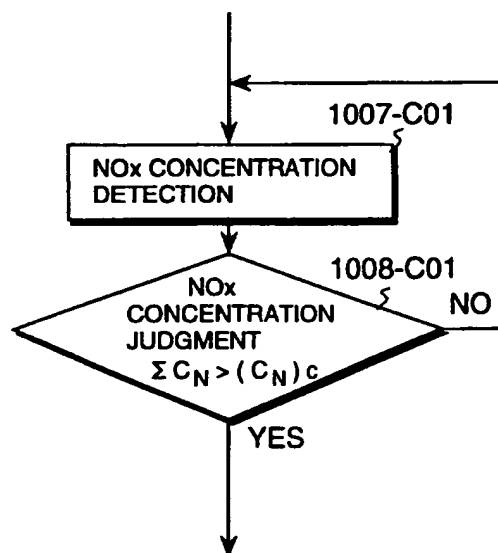




FIG. 15

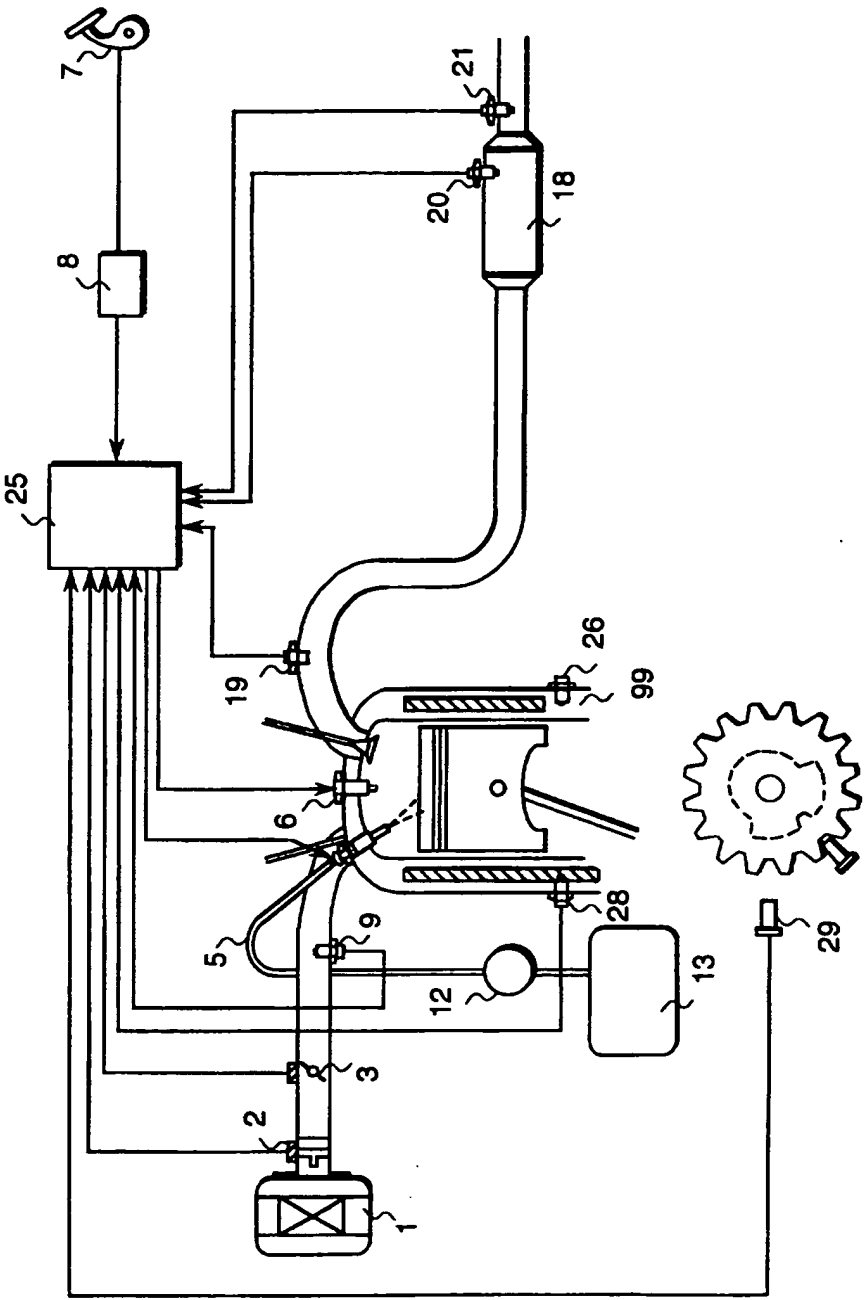


FIG. 16

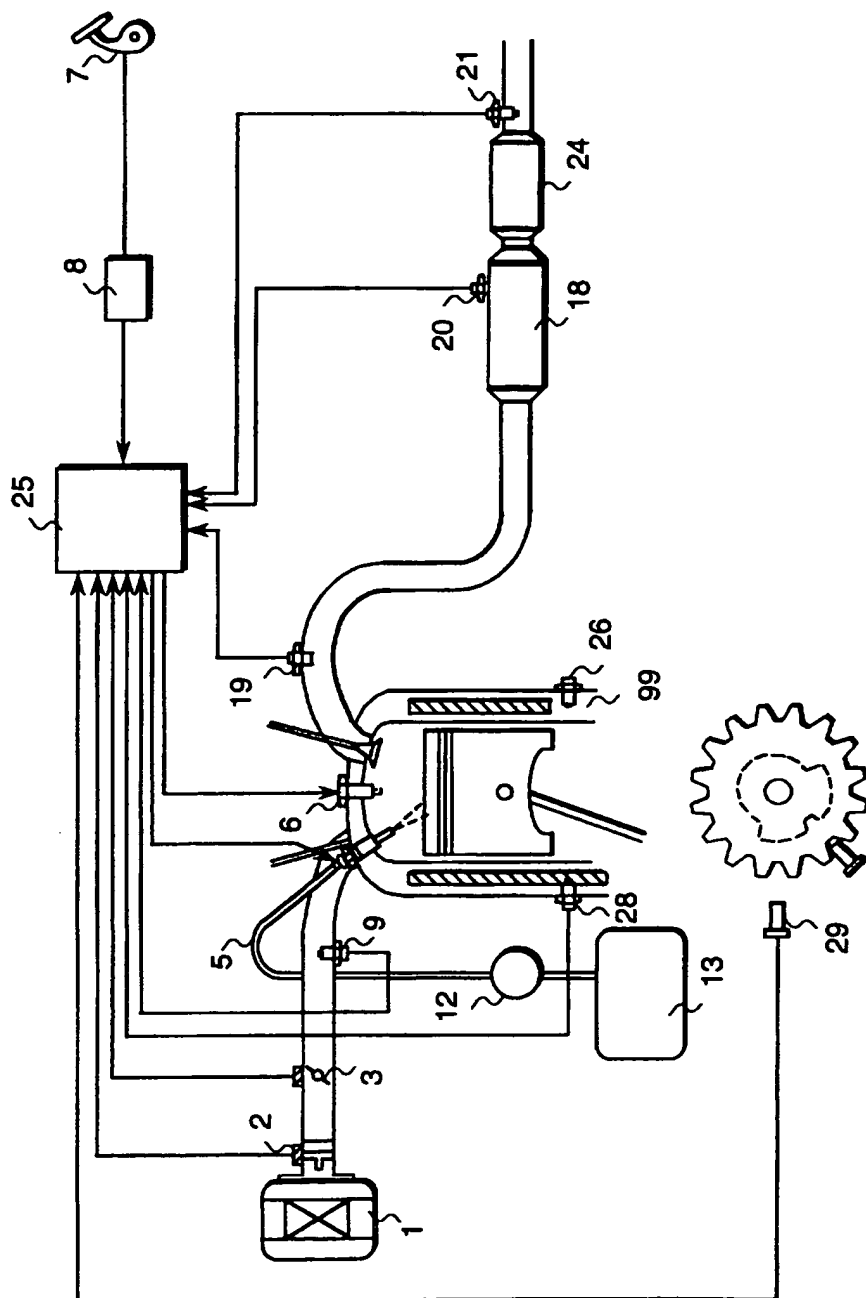
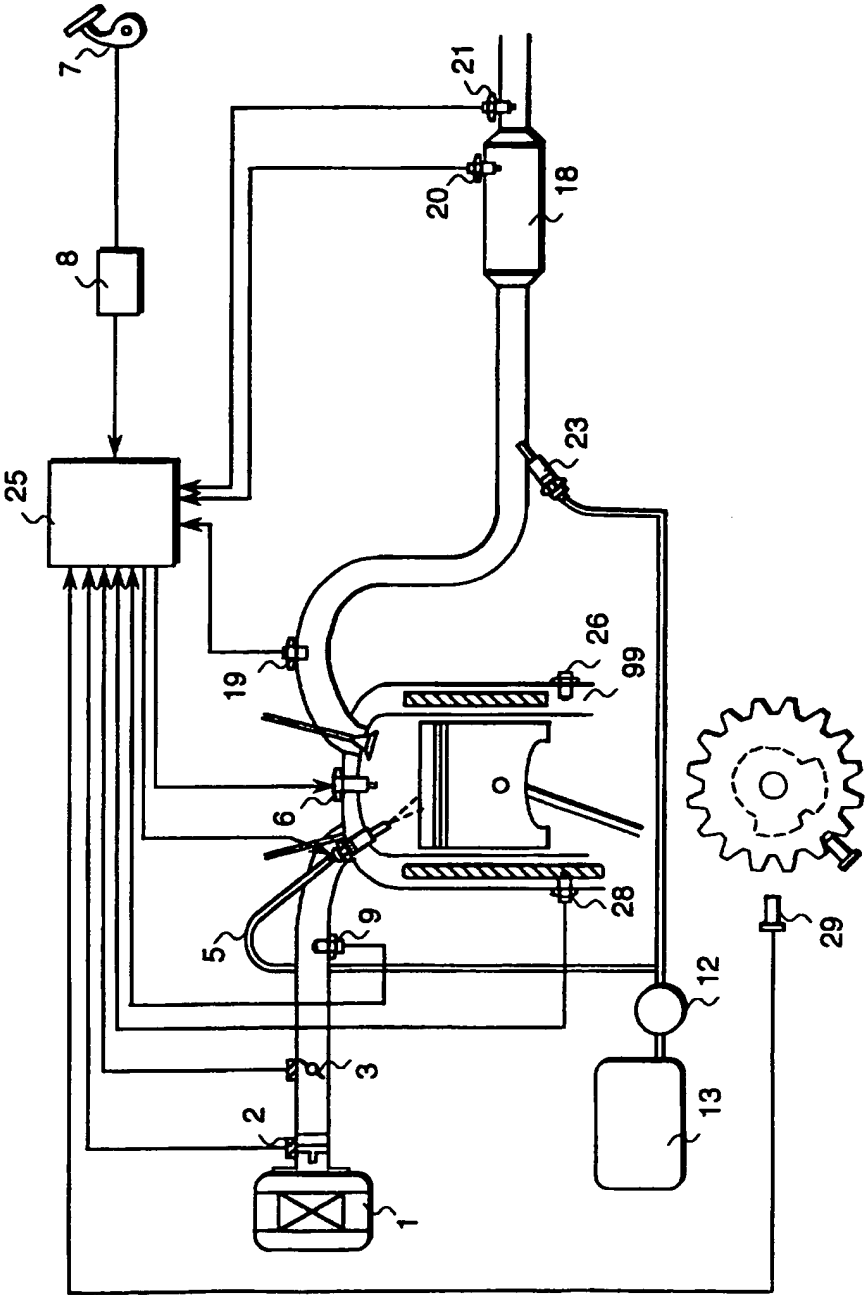
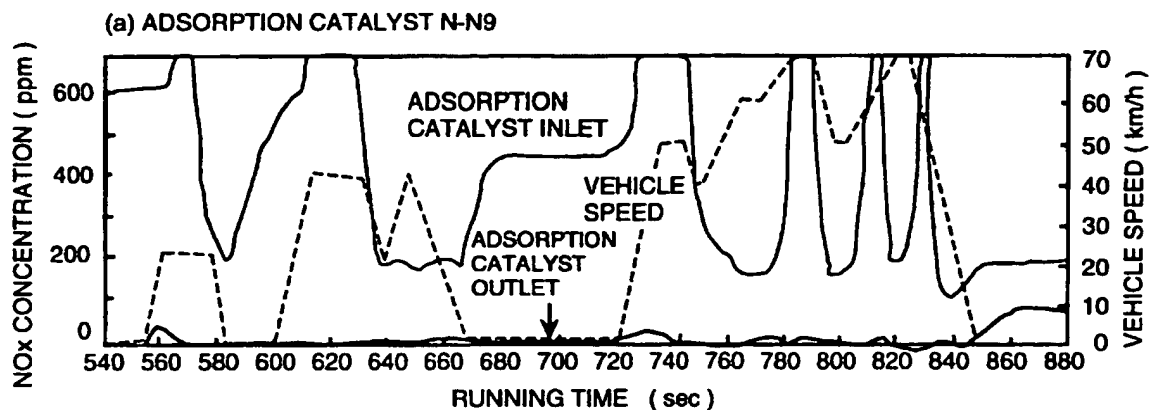
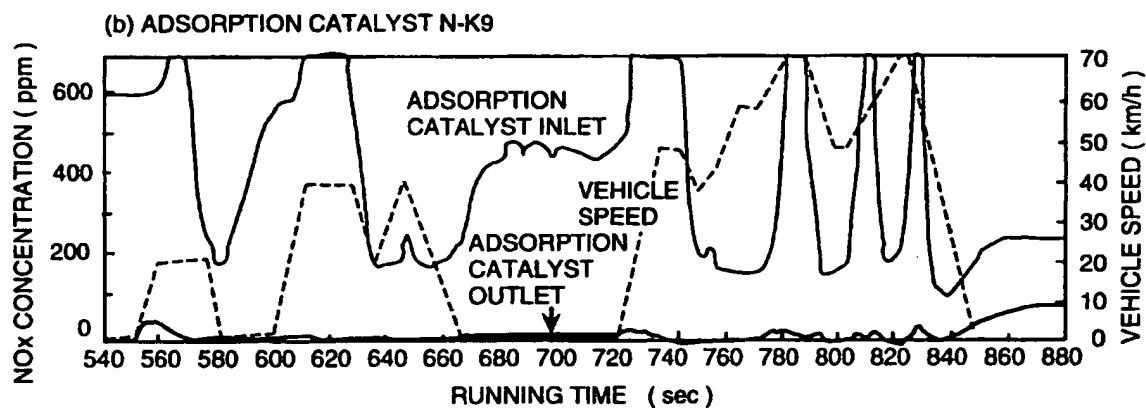
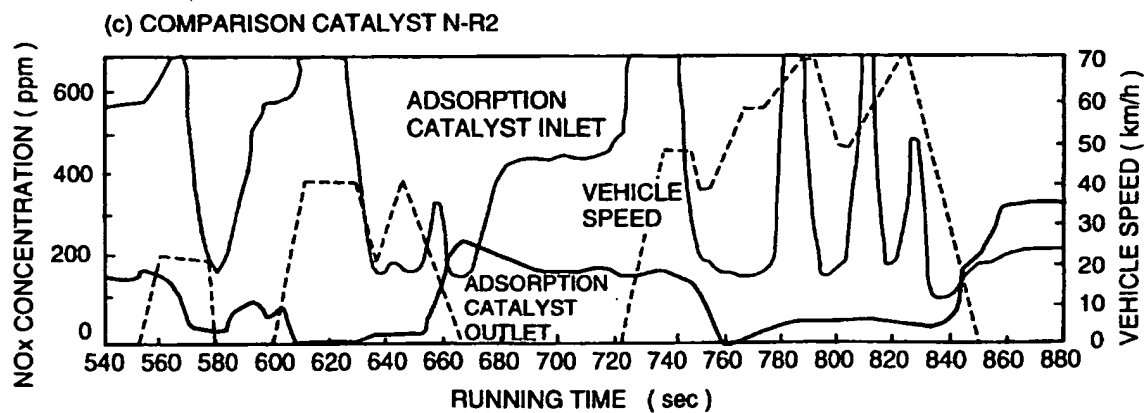




FIG. 17



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**FIG. 18A****FIG. 18B****FIG. 18C**

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FIG. 19

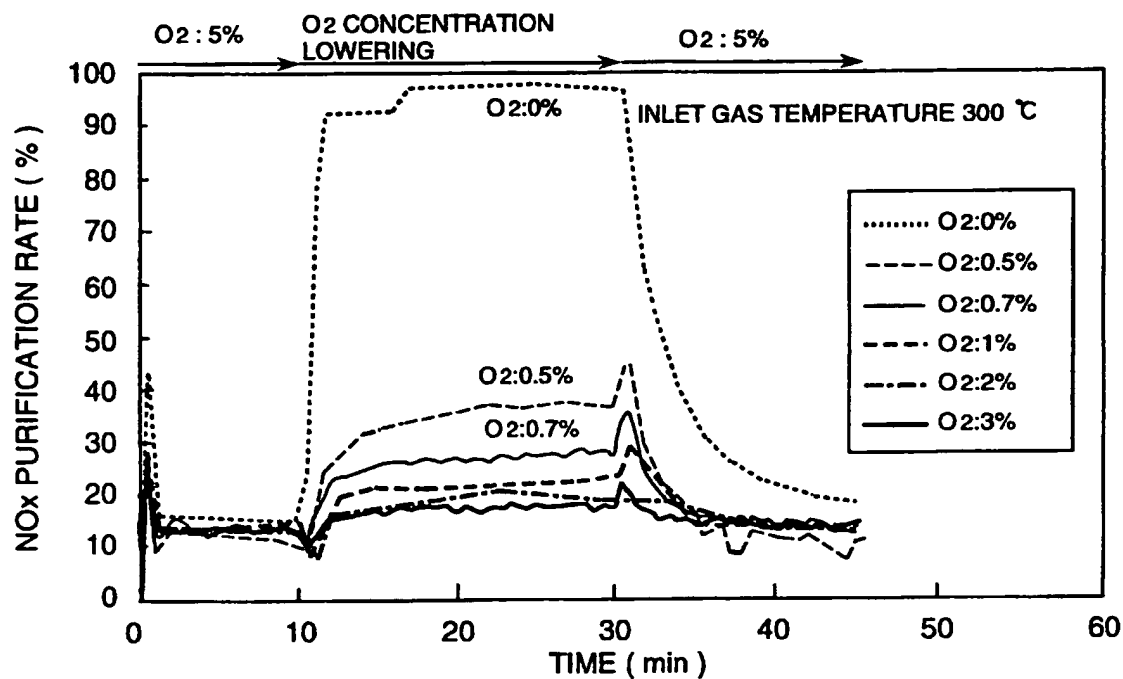
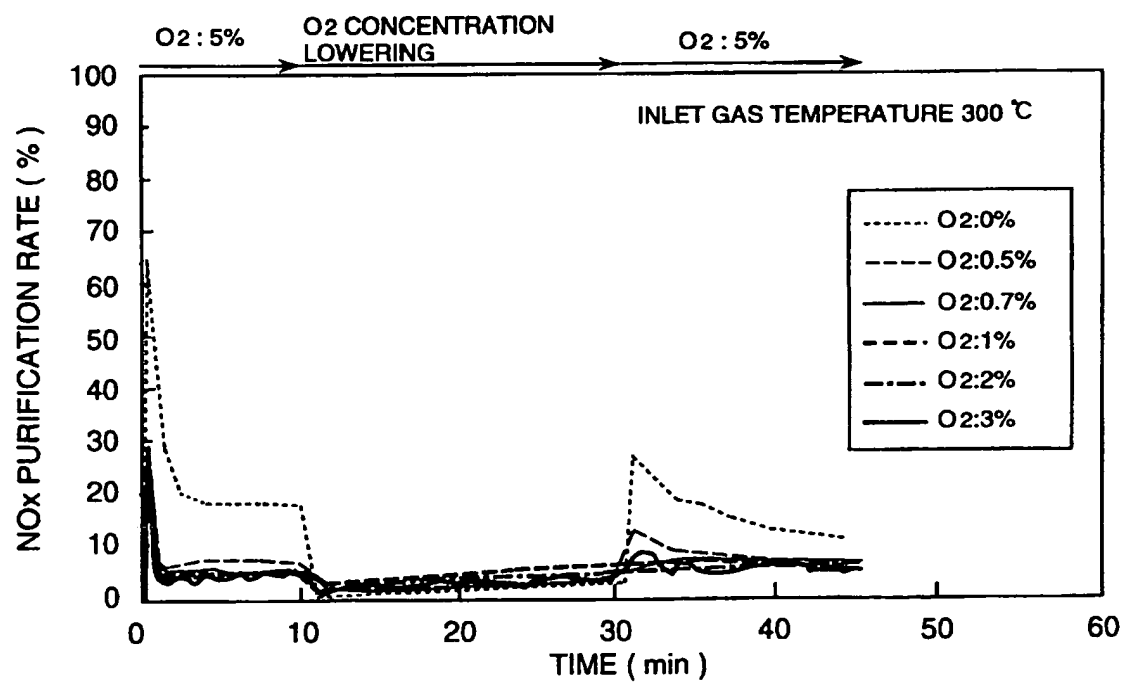


FIG. 20



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FIG. 21

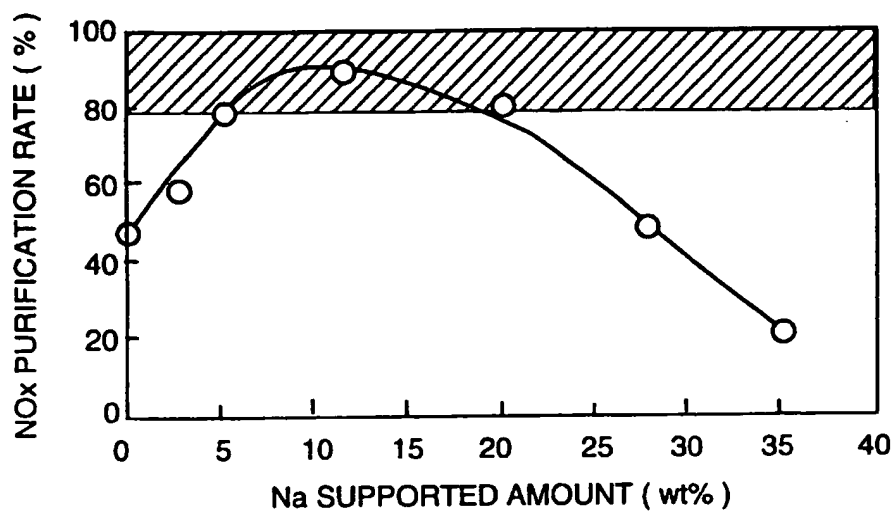
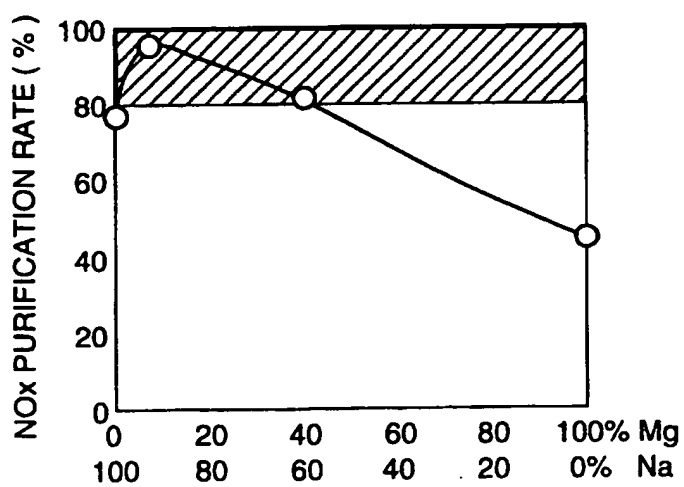


FIG. 22



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FIG. 23

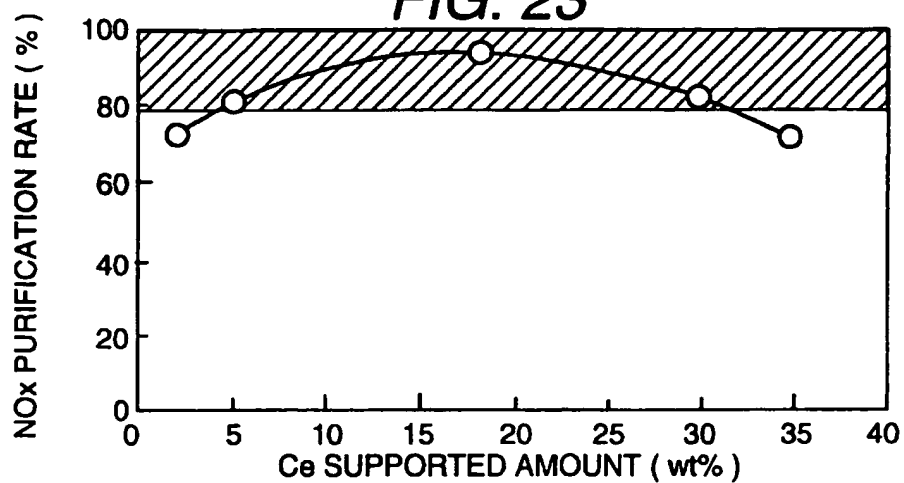
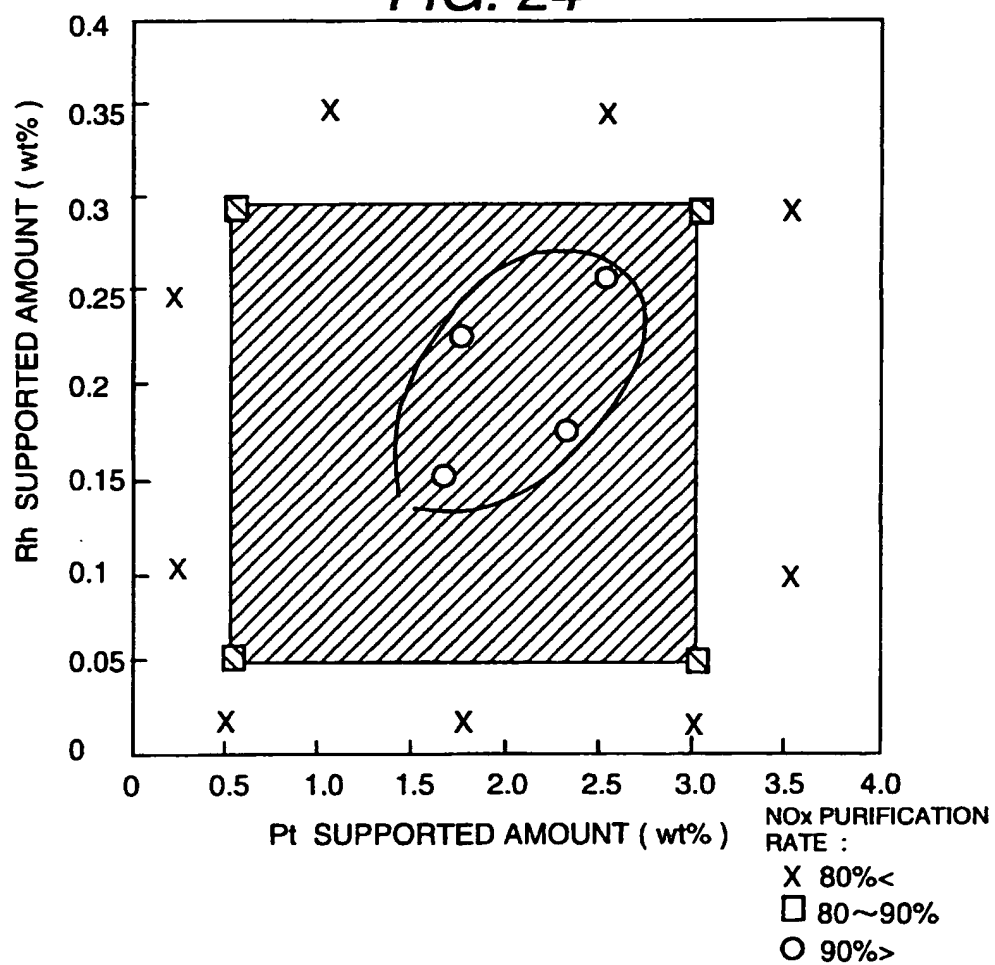


FIG. 24



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FIG. 25

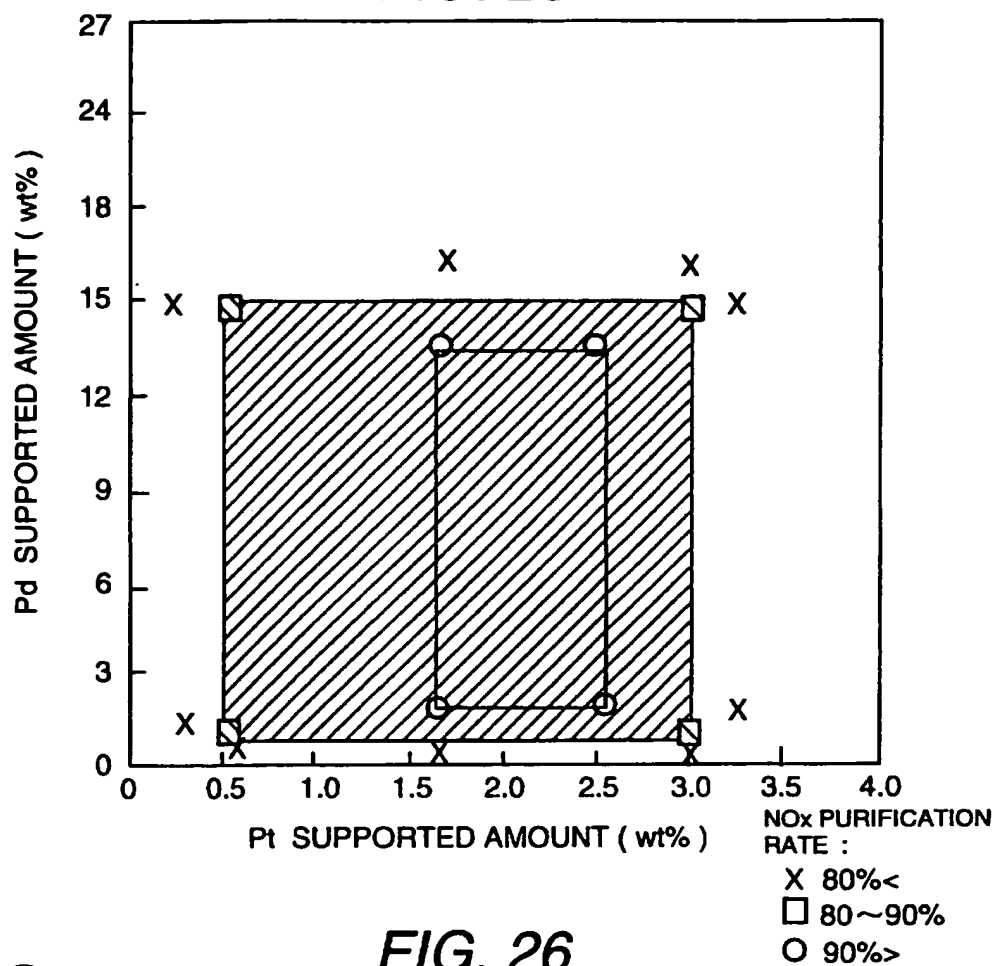
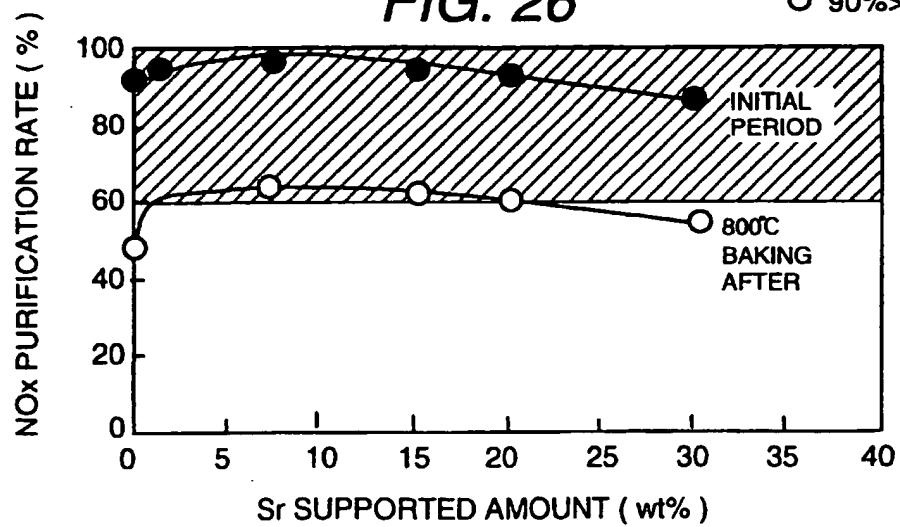


FIG. 26



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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP 97/01955

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC6: F01N 3/20**  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC6: F01N**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5473887 A (SHINICHI TAKESHIMA ET AL), 12 December 1995 (12.12.95) --	1
A	US 5471836 A (SHINICHI TAKESHIMA ET AL), 5 December 1995 (05.12.95) --	1
A	US 5483795 A (KENJI KATOH ET AL), 16 January 1996 (16.01.96), abstract --	1
A	EP 0598916 A1 (TOYOTA JIDOSHA KABUSHIKI KAISHA), 1 June 1994 (01.06.94), abstract -- -----	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

24 Sept 1997

Date of mailing of the international search report

07.11.97

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Authorized officer

Johan von Döbeln

## INTERNATIONAL SEARCH REPORT

Information on patent family members

01/09/97

International application No.

PCT/JP 97/01955

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US 5483795 A	16/01/96	EP 0636770 A WO 9417291 A	01/02/95 04/08/94
EP 0598916 A1	01/06/94	JP 54028254 A US 5450722 A EP 0598917 A JP 2586739 B US 5437153 A WO 9325805 A WO 9325806 A JP 6010725 A	02/03/79 19/09/95 01/06/94 05/03/97 01/08/95 23/12/93 23/12/93 18/01/94